

2016

# Evaluation of Ammonia Volatilization and Zinc Nutrition of Experimental Zinc Sulfate Coated Urea Fertilizers in a Drill-seeded Delayed Flood Rice Production System

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EVALUATION OF AMMONIA VOLATILITY AND ZINC NUTRITION OF  
EXPERIMENTAL ZINC SULFATE COATED UREA FERTILIZERS IN A DRILL-SEEDED,  
DELAYED FLOOD RICE PRODUCTION SYSTEM

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

in

The School of Plant, Environmental and Soil Sciences

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December, 2016

## **Acknowledgements**

I am grateful to God for helping me complete my studies. I would like to thank my major professor, Dr. Dustin L. Harrell for his invaluable encouragement, advice, and guidance. I appreciate the sound inputs, time, and efforts from my dissertation committee members Dr. Jim J. Wang, Dr. Magdi H. Selim, Dr. Rita R. Culross, Dr. Brenda S. Tubana, and Dr. Manoch Kongchum in ensuring the success of this study.

I am very grateful to Dr. Magdi H. Selim for his advice and allowing me access to his laboratory and instruments. I would like to thank the staff of H. Rouse Caffey Rice Research Station and the LSU AgCenter Soil Testing and Plant Analysis Laboratory for their invaluable contributions during my study.

I appreciate the kindness and support from Drs. William and Margaret Forbes throughout all of my graduate studies. Finally, I would like to thank my parents and siblings for their support, out pouring of love, and care beyond description.

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## Abstract

Approaches in controlling nitrogen (N) loss from pre-flood fertilizer applications in delayed flood rice (*Oryza sativa*) production in the mid-southern U.S.A. typically involves treating urea with urease inhibitors like N-(n-butyl) thiophosphoric triamide (NBPT). Limited research exists on managing N utilizing the combined effects of treating urea with a urease inhibitor and subsequently adding a physical zinc (Zn) sulfate coating. Zinc deficiency is also a major soil fertility constraint in flooded rice production. The objectives of this study were to: (i) determine the ammonia volatilization potential of experimental zinc sulfate coated urea (ZSCU) fertilizers on four rice soils in a controlled environment, (ii) quantify ammonia volatilization losses from surface broadcast experimental ZSCU fertilizers under field conditions, (iii) evaluate the effect of experimental ZSCU fertilizer use as an N source in rice production, and (iv) evaluate experimental ZSCU fertilizer as a Zn fertilizer source in rice production. Experimental ZSCU fertilizers used in the controlled environment study and field trial included; RCO3, RCO2, RCO5, RCO1, RCO4, RCO1S and RCO4S. To evaluate ZSCU as a Zn source, five preplant and four pre-flood Zn fertilizer treatment combinations were evaluated alongside the control and the recommended practice of applying granular Zn sulfate. In comparison to urea, application of experimental ZSCU and urea treated with NBPT in the controlled experiment reduced ammonia loss 14 – 81 and 27 – 64%, respectively, across all soils. Cumulative ammonia loss from RCO4 and RCO4S was comparable to the NBPT-urea at a rate of 0.9 g NBPT kg<sup>-1</sup> (w/w). Cumulative ammonia losses from the field trial ranged from 3.1–15.1 and 5.4 –22.5% in 2014 and 2015, respectively. Cumulative ammonia loss from ZSCU fertilizers was significantly lower than urea but greater than urea treated with NBPT in both years. Urea treated with NBPT out yielded all other N fertilizers in 2015. Experimental ZSCU fertilizers, particularly those containing B and

NBPT, did reduce ammonia volatilization in soils susceptible to ammonia volatilization; however, the effect in controlling ammonia volatilization did not result in increased rice yield. The experimental ZSCU was similar to surface broadcast Zn sulfate alone, despite the improved distribution when applying similar rates.

## **Chapter 1. General Introduction**

### **1.1 Introduction**

Nitrogen (N) is the most important fertilizer nutrient for optimizing rice (*Oryza stiva*) grain yield potential. Urea and ammonium sulfate are the most commonly used N fertilizers for pre-flood fertilizer applications in the mid-southern United States (Norman et al., 2009; Rogers et al., 2015). Urea is the preferred N fertilizer source due to its relative low cost, its high N content (46%), and ease in handling. A 1:1 blend of urea and ammonium sulfate is also often used for pre-flood N fertilization in rice (Griggs et al., 2007; Dillion et al., 2012). The blend between the two N sources improves crop N efficiency as compared to urea alone; however, the lower N content of blended fertilizer (33%) and its higher cost per kilogram of N discourages its use (Harrell and Saichuk, 2016). Fertilizer N in rice is surface broadcast at the 4- to 5-leaf stage of rice development (pre-flood N fertilization) and the remainder is applied mid-season between the panicle initiation and panicle differential stages of development. When pre-flood N fertilizer applications are left on the soil surface for an extended period of time prior to flooding much of the N can be lost due to ammonia volatilization and subsequent nitrification/denitrification (Craswell and Vlek, 1979).

Surface broadcast urea is hydrolyzed to ammonium bicarbonate in the presence of the urease enzyme and favorable environmental conditions (Wahl et al., 2006). The bicarbonate raises soil pH, creating an ideal condition for rapid conversion of ammonium to ammonia which escapes into the atmosphere (Mikkelsen et al., 1978; Craswell and Vlek, 1979; Griggs et al., 2007). Ammonia volatilization has been documented as the primary N loss pathways from surface broadcast pre-flood urea fertilization (Reddy, 1982; Keeney and Sahrawat, 1986; Francis et al., 2012). Ammonia volatilization may account for 24 – 80% loss from surface broadcast

preflood urea applications in rice depending on management practices and prevailing environmental conditions during and following application (Cai et al., 2002; Francis et al., 2008; Norman et al., 2009; Griggs et al., 2007; Dillion et al., 2012). Substantial loss of N as ammonia has the potential to limit rice productivity and contribute to atmospheric pollution (Janssens et al., 2010; Phoenix et al., 2012). Controlling ammonia volatilization in rice production greatly improves the efficiency of N preflood urea, increases grain yield, and protects the environment (Francis et al., 2012; Phoenix et al., 2012).

Ammonia volatilization from surface broadcast urea has been a concern for decades and several efforts have been made with regard to the development and implementation of strategies to control ammonia volatility (Bremner and Chai, 1989; Al-Kanani et al., 1994; Rawluk et al., 2001). Ammonia volatilization can be influenced by management practices, soil properties, and prevailing weather conditions during and after N fertilizer application (Aneja et al., 2000a). The environmental factors are often interrelated and not clearly distinguish under field conditions. Management practices are factors that are constantly being manipulated to control ammonia volatilization. Some of these practices have been successful, to a varying extent, in decreasing ammonia volatilization. Management practices that commonly influence ammonia volatilization are water management, timing of fertilization, fertilizer source, and additional modifications of the fertilizer source (Jones et al., 2007; Jones et al., 2013). Studies have shown that establishing a permanent flood within 3 d after preflood N fertilization can effectively reduce volatilization (De Datta and Patrick, 1986; Savin et al., 2007). Norman et al. (2009) reported that the amount of ammonia loss when the flood is delayed 5 d after preflood N fertilization is more than twice the loss observed compared to 2 d after fertilization. Establishing permanent flood in a timely manner is impossible for many commercial farms as result of irrigation constraints. On average,

it may take 10 d for many commercial fields to establish a permanent flood. Incorporating and surface banding of urea are effective means of suppressing ammonia volatilization; however, these practices are not feasible in rice production systems. Blending urea with KCl or  $\text{CaCl}_2$  has been reported to reduce ammonia volatilization from surface broadcast urea (Al-Kanani et al., 1994).

Current strategies employed in controlling ammonia volatilization focus on modifying urea fertilizers to slow down urea hydrolysis (Trenkel, 2010; Timilsena et al., 2015). These modified urea fertilizers are characterized as enhanced efficiency nitrogen fertilizers (EENF). Enhanced efficiency nitrogen fertilizers are prepared by chemically treating urea with urease inhibitors or physically coating urea with another fertilizer nutrient or polymer. Urea treated with urease inhibitors have been documented as an effective strategy to reduce ammonia volatilization from surface broadcast urea (Bremner and Chai, 1989; McCarty et al., 1989; Watson, 2000). Urease inhibitors may disrupt the function of the urease enzyme through following modes: (1) chelating compounds that cause inhibition due to complex formation with one of the nickel (Ni) atoms at the active site of urease, and (2) competitive inhibitors that resemble urea molecules and bind to the active site of the urease enzyme (Amtul et al., 2002). Several chemicals and metals have been evaluated as potential urease inhibitors (Clay et al., 1990; Amtul et al., 2002). Among the chemicals evaluated, N-(n-propyl) thiophosphoric acid triamide (NPPT) and N-(n-butyl) thiophosphoric triamide (NBPT) have been identified as effective in reducing ammonia volatilization (Engel et al., 2011; Griggs et al., 2007; Dillon et al., 2012). The most commonly used urease inhibitor in rice production is NBPT, because of its effectiveness across different soil types and cropping systems (Bremner and Chai, 1989; Al-Kanani et al., 1994; Rawluk et al., 2001; Tian et al., 2015). Rawluk et al. (2001) reported that the use of  $0.05 - 0.15 \text{ g kg}^{-1}$  NBPT

(w/w) reduced total ammonia loss by 28 – 88% over 21 d. Norman et al. (2009) reported that cumulative ammonia volatilization decreased by more than 50% two weeks after fertilization. Engel et al. (2011) reported that urea treated with 0.1 g kg<sup>-1</sup> NBPT reduced cumulative ammonia losses by 66%. Studies have reported that sulfate compounds of metals, such as Zinc (Zn) and Copper (Cu); can decrease ammonia volatilization (Bremner and Douglas, 1971; Reddy and Sharma, 2000). Boric acid and other boron (B) compounds have also been cited as urease inhibitors (Tabataba, 1977; Benini et al., 2004; Singh et al., 2013; Pursell et al., 2014).

Urea coated with nutrient or polymers were developed primarily to supply N gradually over the growing season, but studies have reported the inhibitory effect of these fertilizers on ammonia volatilization (Xu et al., 2012). Physical coatings decrease the urea surface area for urease attack, thus slow down urea hydrolysis and subsequently minimizing the rate of ammonia volatilization. Reduction in ammonia volatilization from polymer-coated urea fertilizers has been documented on rice fields (Tian et al., 2015). Nutrient-coated urea, such as sulfur coated urea, has been documented to reduce ammonia volatilization (Jantalia et al., 2012). However, the inhibitory effects of polymer- and nutrient-coated urea fertilizers on ammonia volatilization are inconsistent across cropping systems and soil types (Tian et al., 2015).

Zinc deficiency is the most documented micronutrient deficiency in flooded rice fields in the mid-southern United States (Slaton et al., 2005a). In most cases, seedling rice that exhibit Zn deficiency symptoms will have a delay in maturity and subsequent reduction in grain yield, particularly for susceptible cultivars. In severe cases, the entire rice stand may be lost. Plant breeding offers a cost effective approach to improve Zn deficiency. Currently, the use of fertilizers is the best possible solution to ameliorating Zn deficiency. Zinc deficient rice fields are commonly ameliorated with Zn sulfate, Zn chelates (Zn-EDTA, Zn-NTA), and products from



natural organic ligands (Mikkelsen and Kuo, 1977; Slaton et al., 2005). Zinc sulfate is very soluble and highly bioavailable when applied initially; however, their bioavailability declines with time because it can be transformed into insoluble Zn forms. Organic Zn fertilizer sources have been documented to increase grain yield and tissue Zn concentration; however, their high cost limits their use and application (Slaton et al., 2005).

## **1.2 Justification**

Louisiana ranks as the third highest rice-producing state in the U.S.A., accounting for 15% of total rice production in 2015 (USDA, 2016). Approximately two-thirds of rice is cultivated in the southwest region of Louisiana covering Acadia, Allen, Calcasieu, Cameron, Evangeline, Jefferson Davis, St. Landry, and Vermilion parishes (Salassi and Deliberto, 2013). Common soil fertility constraints associated with flooded rice production in these regions are low N use efficiency and Zn deficiency (Harrell and Saichuk, 2016). The low N use efficiency has been partly attributed to ammonia volatilization. Studies conducted in Louisiana have shown ammonia volatilization losses from surface applied urea after 10 d generally range from 17 – 33% (Dillion et al., 2012). The dominant coastal prairie soils in southwest Louisiana are characterized by inherently low Zn and hence its deficiency is a common occurrence (Weindorf, 2008). Flooding decreases Zn availability for rice uptake (Rehman et al., 2012). Zinc deficiencies have been further compounded by cultivating high yielding rice varieties, increased adoption of laser leveling techniques, and improved purity of inorganic fertilizers (Brye, 2006). A cost effective fertilizer, such as one of the experimental Zn sulfate coated urea fertilizers (ZSCU) which can simultaneously reduce ammonia volatilization and correct Zn deficiency would be extremely valuable to the mid-southern commercial rice industry.

Several strides have been examined to effectively control ammonia volatilization by treating urea with a urease inhibitor or coating urea with a nutrient or polymer independently. However, current efforts are aimed at developing urea fertilizers that combine urease inhibitor and physical coatings (Frame et al., 2012). This ammonia control strategy includes the addition of micronutrients as a surface coating on a urea granule which improves the distribution of micronutrients that are only required by plants in minute quantities. Combining a low concentration of NBPT with B in addition to a nutrient coating on urea, may improve the reliability of the nutrient coated urea fertilizer to effectively minimize ammonia volatilization and increase rice productivity. Experimental ZSCU fertilizers with or without urease inhibitors have been recently developed (Brooks Whitehurst Associates Inc., New Bern, NC). The urease inhibitors contained in some of these experimental ZSCU fertilizers included NBPT and/or B. No study has quantified ammonia volatilization and grain yield potential of Zn sulfate coated urea in combination with NBPT and/or B fertilizer in delayed flood rice production systems.

### **1.3 Objectives**

The overall objective of this study was to investigate experimental ZSCU fertilizers as an alternate strategy for controlling ammonia volatilization and as a Zn fertilizer source in rice. The specific objectives were to: (i) determine the ammonia volatilization potential of urea, urea treated with three rates of NBPT, and four experimental ZSCU fertilizers on four rice soils at 2/3 field capacity in a controlled environment, (ii) quantify ammonia volatilization losses from surface broadcast experimental ZSCU fertilizers under field conditions, (iii) evaluate the effect of experimental ZSCU fertilizers as an N source on biomass, N uptake, nitrogen use efficiency, and grain yield in a delayed flood rice production system, and (iv) evaluate experimental ZSCU fertilizer as Zn fertilizer source in a delayed flood rice production system.

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## **Chapter 2. Volatilization Potential of N-(n-butyl) Thiophosphoric Triamide (NBPT)**

### **Treated Urea and Zinc Sulfate Coated Urea Fertilizers**

#### **2.1 Introduction**

Urea and ammonia sulfate fertilizers are commonly used for pre-flood nitrogen (N) fertilization in commercial rice (*Oryza sativa*) production in the mid-southern United States (Norman et al., 2009; Harrell et al., 2015). Urea is preferred to ammonium sulfate due to its lower cost per kilogram of N despite its susceptibility to ammonia volatilization (Griggs et al., 2007; Junejo et al., 2011). Ammonia volatilization from surface applied pre-flood urea fertilizer in delayed-flood rice production is well documented in the mid-southern United States (Norman et al., 2009; Dillion et al., 2012). Volatility losses of 24 – 80% of the total applied N from pre-flood urea applications in rice have been reported (Cai et al., 2002; Sommer et al. 2004; Griggs et al., 2007; Francis et al., 2008; Norman et al., 2009; Dillion et al., 2012; Behera et al., 2013). Excessive gaseous losses from pre-flood N fertilizer applications are agronomically and economically detrimental for commercial rice farmers (Singh et al., 2012). Nitrogen loss as ammonia can be curtailed with appropriate fertilizer management practices, such as establishing flooded fields in a timely manner (Savin et al., 2007). However, this practice is not plausible in many large commercial rice fields mainly due to irrigation constraints.

Currently, novel approaches to minimizing ammonia volatility have centered on treating or physically coating urea fertilizers to temporarily halt urea hydrolysis. Incubation studies showed that simultaneous application of urea and potassium chloride (KCl) reduced ammonia volatilization from 46 to 4.5% (Rapport and Axley, 1984; Gameh et al., 1990; Reddy and Sharma, 2000). Modified urea fertilizers such as these are often referred to as enhanced efficiency nitrogen fertilizers (EENF) (Trenkel, 2010). Enhanced efficiency nitrogen fertilizers

have been shown to offer agronomic, economic, and environmental benefits over urea fertilizers (Rawluk et al., 2001; Golden et al., 2011; Timilsena et al., 2015).

Urease inhibitors used in combination with urea as EENF have long been recognized as an effective strategy to suppress ammonia volatilization from surface applied urea. The most commonly used urease inhibitor is N-(n-butyl) thiophosphoric triamide (NBPT). This urease inhibitor works by forming a complex with one of the nickel (Ni) atoms at the active site of the urease enzyme (Amtul et al., 2002). The efficacy of NBPT in mitigating volatilization is well documented for various agricultural crops and field situations (Griggs et al., 2007; Engel et al., 2011; Dillion et al., 2012). Rawluk et al. (2001) reported that the use of 0.05 – 0.15% NBPT reduced total ammonia loss by 28 – 88% over 21 d. Norman et al. (2009) reported that cumulative ammonia volatilization decreased by more than 50% two weeks after fertilization. Engel et al. (2011) reported that urea treated with 0.1% NBPT reduced cumulative ammonia losses by 66%.

Other approaches to reducing the potential for ammonia volatilization besides organic urease inhibitors have included inorganic urease inhibitors and physical coating. Studies have reported that sulfate compound of metals, such as Zn and Cu; can decrease ammonia volatilization (Bremner and Douglas, 1971; Reddy and Sharma, 2000). Boric acid and other boron compounds have also been cited as urease inhibitors (Tabataba, 1977; Benini et al., 2004; Singh et al., 2013; Pursell et al., 2014). Urea with nutrient and polymer coatings, commonly referred to as controlled release fertilizers, are manufactured primarily to synchronize N release to meet a plant's N demand. Polymer and nutrient coatings can temporally reduce ammonia volatilization of urea (Trenkel, 2010; Timilsena et al., 2015). Black et al. (1985) reported a 20% reduction in ammonia volatilization from a sulfur coated urea fertilizer.



Soil moisture content plays an important role in urea hydrolysis and subsequently ammonia volatilization (Bock and Kissel, 1988; Lui et al., 2007; Rochette et al., 2009a). Ammonia volatility potential is maximized when the soil moisture content is at or near field capacity (Bouwmeester et al., 1985). Field capacity (FC) is the measure of water retained by the soil matrix at 33 kPa of suction (Bell and Van Keulen, 1996). Field capacity can be accurately predicted from a soil moisture characteristic curve (SMCC) which describes the relationship between wetness and matric potential using various mathematical models (Hillel, 2004). Soil wetness refers to gravimetric or volumetric moisture content of the soil. The SMCC for undisturbed core samples does not only predict FC but can also be a reliable predictor of moisture behavior of a soil across a wide range of suction values experienced in the field. Thus, the SMCC predicts the soil water storage and availability for plant uptake and fertilizer decomposition. Soil properties such as texture, structure, and organic matter content influence the shape of the soil moisture characteristic curve. As such, the moisture content and behavior of soils in the same soil order and textural class may differ. For example, moisture retained at low suction ( $< 100$  kPa) values is primarily influenced by soil structure while higher suction values are primarily influenced by soil texture and specific surface area (Hillel, 2004). Limited studies have been conducted to evaluate ammonia volatilization potential from rice paddy soils based on equivalent soil moisture content determined from a SMCC.

Several advances have been made to minimize ammonia volatilization by chemical and physical means independently; however, efforts are also being made to develop N fertilizers that simultaneously utilize multiple approaches to address ammonia volatilization as well as other nutritional deficiencies often encountered in crop production (Frame et al., 2012). This multipronged approach often includes the addition of a micronutrient compound as a surface

coating, which can reduce ammonia volatilization and also improve the distribution of the micronutrient. Most approaches at controlling ammonia volatilization in commercial rice production in the mid-southern U.S. involve only the use of a urease inhibitor applied onto urea, namely NBPT. The potential synergic effect of urea treated with NBPT and subsequently coating it with a micronutrient has not been extensively explored. Therefore, preliminary research is needed to evaluate the volatility potential of NBPT treated urea used in combination with a micronutrient coating in a controlled laboratory environment prior to further testing in field trials. The objectives of this study were to (i) determine soil moisture, chemical, and physical characteristics of four common mid-southern United States rice soils, and (ii) determine the ammonia volatilization potential of urea, urea treated with three rates of NBPT, and four experimental zinc sulfate coated urea (ZSCU) fertilizers on four rice soils at 2/3 field capacity in a controlled environment.

## **2.2 Materials and Methods**

### **2.2.1 Experimental Soils**

Four soils from rice fields in southwest Louisiana were selected for the trials based on varying soil physical or chemical characteristics. The soils included Kinder silt loam (Fine, silty, siliceous, active, thermic Typic Glossaqualfs; N 30° 16.521' W 92°), Mowata silt loam (Fine smectitic, thermic, Typic Glossaqualfs; N 30° 38.820' W 92° 30.585), and two Crowley silt loam (Fine smectitic, thermic, Typic Albaqualfs) soils. The two Crowley silt loam soils differed in surface texture of the top 15 cm and pH and are referred to as Crowley H (N 30° 16.88' W 92° 25.083; silt; pH 7.4) and Crowley L (N 30° 14.840' W 92° 21.196; silt loam; pH 6.6) in this trial. Composite soil samples were collected from surface soil to a depth of 15 cm. The soils were air dried, sieved through a 2 mm sieve, and analyzed for selected chemical and physical properties.

Soil pH was analyzed using a 1:1 soil to water ratio (Thomas, 1996). Total soil N and C were determined by dry combustion analysis using a LECO TruSpec CN analyzer (LECO, Corp., St. Joseph, MI). The particle size distribution and field capacity of soils were determined using the hydrometer and pressure plate methods, respectively (Gee and Or, 2002; Topp and Ferré, 2002). Cation exchange capacity was determined by Kjeldahl distillation using ammonium acetate method (Sumner and Miller, 1996). Nutrients were extracted with the Mehlich III and Diethylenetriaminepentaacetic acid (DTPA) solutions, respectively (Mehlich, 1984; Lindsay and Norvell, 1978). Elemental concentrations in the extracts were measured using inductively coupled plasma atomic emission spectroscopy. Mean values of selected chemical and physical soil properties are presented in Tables 2.1 and 2.2, respectively.

#### 2.2.2 Soil Moisture Characteristic Curve

The SMCCs of the soils were determined using the pressure plate procedure (Topp and Ferré, 2002). Undisturbed core samples (5 cm in diameter and 2 cm thick) were collected from the top 6 cm of the soil surface. The soil cores were trimmed at both ends to ensure maximum surface contact. Undisturbed core samples were saturated on porous ceramic plates for one week and then transferred to the pressure plate apparatus. Suction was applied at nine different levels incrementally (10, 30, 50, 75, 100, 300, 1000, and 1500 kPa) encompassing the important moisture range for agricultural soils (33 and 1500 kPa for FC and wilting point, respectively). Four replicates were used for each soil at a given suction. After the final suction (1500 kPa), the core samples were oven dried at 105°C to quantify the volumetric moisture content and bulk density. The van Genuchten (1980) equation was used to fit the experimental data using Sigma plot (Systat Software, San Jose, CA).

Table 2.1 Chemical properties of Crowley H, Crowley L, Kinder, and Mowata silt loam soils (0-15 cm).

Soil <sup>†</sup>	pH	CEC <sup>‡</sup>	OM <sup>§</sup>	C	N	Mehlich III extractable						DTPA extractable			
						P	K	Ca	Mg	Na	S	Cu	Zn	Fe	Mn
		cmol <sub>c</sub> kg <sup>-1</sup>				g kg <sup>-1</sup>						mg kg <sup>-1</sup>			
Crowley L	6.6	5.8	15	8.4	1.0	16	89	1367	238	58	8.3	1.0	4.4	58	47
Crowley H	7.4	13.3	21	10.8	1.2	73	89	2522	430	109	6.3	1.0	6.4	158	19
Kinder	6.6	6.6	15	8.5	0.8	7.4	83	1083	163	52	8.7	1.1	6.9	99	49
Mowata	5.8	6.1	11	6.2	0.6	4.4	69	809	192	50	9.3	0.6	11	46	76

<sup>†</sup>Crowley L, Crowley silt loam (pH 6.6); Crowley H, Crowley silt loam (pH 7.4).

<sup>‡</sup>CEC, cation exchange capacity.

<sup>§</sup>OM, Organic matter.

Table 2.2 Physical properties of Crowley H, Crowley L, Kinder, and Mowata silt loam soils (0-15 cm).

Soil <sup>†</sup>	Sand	Silt	Clay	Texture <sup>‡</sup>	Bulk density	FC <sup>§</sup>
	g kg <sup>-1</sup>				g cm <sup>-3</sup>	cm <sup>3</sup> cm <sup>-3</sup>
Crowley L	41	802	157	SL	1.39	0.36
Crowley H	33	860	107	S	1.34	0.39
Kinder	84	784	132	SL	1.46	0.38
Mowata	164	614	222	SL	1.49	0.29

<sup>†</sup>Crowley L, Crowley silt loam (pH 6.6); Crowley H, Crowley silt loam (pH 7.4).

<sup>‡</sup>Texture, USDA textural class.

<sup>§</sup>FC, Field capacity; FC was determined at 33 kPa using the pressure plate procedure (Topp and Ferré, 2002).

The van Genuchten equation can be expressed as:

$$\Theta(h) = \theta_r + \frac{(\theta_s - \theta_r)}{(1 + (\alpha h)^n)^m} \quad [1]$$

where  $\theta_s$  and  $\theta_r$  represents saturated and residual moisture content, respectively, and  $\alpha$ ,  $n$ , and  $m$  are parameters directly dependent on the shape of curve. The van Genuchten parameters for each soil are presented in Table 2.3. Soil water suction was plotted on a logarithmic normal scale since it extends over several orders for the range of volumetric moisture content measured in this study. Soil moisture concentration was also determined independently from the SMCCs at 33 kPa (FC) for all soils and is presented in Table 2.3.

Table 2.3 van Genuchten equation parameters for Crowley H, Crowley L, Kinder, and Mowata silt loam soils (0 – 6 cm).

Soil <sup>†</sup>	Van Genuchten equation parameters <sup>‡</sup>			
	$\alpha$	$n$	$\theta_r$	$\theta_s$
	cm <sup>-3</sup>		-----cm <sup>3</sup>	cm <sup>-3</sup> -----
Crowley L	0.009	1.47	0.100	0.47
Crowley H	0.006	1.53	0.123	0.48
Kinder	0.009	1.47	0.100	0.47
Mowata	0.012	1.39	0.061	0.43

<sup>†</sup>Crowley L, Crowley silt loam (pH 6.6); Crowley H, Crowley silt loam (pH 7.4).

<sup>‡</sup> $\alpha$  and  $n$ , fitting coefficient;  $\theta_r$ , residual moisture content;  $\theta_s$ , saturated moisture content.

## 2.2.2 Fertilizer Treatments

Eight N fertilizers were evaluated. Fertilizer N sources included urea, urea treated with three rates of NBPT (0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT which corresponds 0.33, 0.5, and 1 times the labeled application rate (ArboriteAg, Weyerhaeuser Company), and four experimental ZSCU fertilizers. The experimental ZSCU fertilizers were manufactured by Brooks Whitehurst Associates Inc. They were identified as RCO3, RCO5, RCO4 and RCO4S. RCO3 was urea with a Zn sulfate coating. RCO5 was urea coated with Zn sulfate with an additional binding agent

containing 1.7 g kg<sup>-1</sup> B. RCO4 was urea which was first treated with 0.6 g kg<sup>-1</sup> NBPT and then coated with Zn sulfate using a binder with 1.7 g B kg<sup>-1</sup>. RCO4S was similar to RCO4 except it had an additional coating of calcium sulfate after the NBPT was treated on the urea and prior to the addition of the Zn sulfate coating. The elemental composition and concentration of the experimental fertilizers are presented in Table 2.4.

Table 2.4 Elemental composition and concentration of experimental zinc sulfate coated urea (ZSCU) fertilizers.

ZSCU <sup>†</sup>	N	P	Ca	S	B	Zn	NBPT <sup>‡</sup>
	-----g kg <sup>-1</sup> -----						
RCO3	389.5	54.0	0.0	12.0	0.0	20.0	0.0
RCO4	392.2	55.0	0.0	11.0	1.7	20.0	0.6
RCO5	392.2	55.0	0.0	11.0	1.7	20.0	0.0
RCO4S	392.2	55.0	3.0	11.0	1.7	20.0	0.6

<sup>†</sup>ZSCU, Zinc sulfated coated urea; RCO3, ZSCU only; RCO4, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT; RCO4S, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT+ CaSO<sub>4</sub> coating; RCO5, ZSCU + 1.7 g B kg<sup>-1</sup>

<sup>‡</sup>NBPT, N-(n-butyl) thiophosphoric triamide.

#### 2.2.4 Ammonia Volatilization Study

The laboratory volatilization study was carried out at the H. Rouse Caffey Rice Research Station in Crowley, Louisiana. Ammonia volatilization from each of the four soils was evaluated in four separate trials. Four environment regulated boxes containing six glass chambers were used for each trial. The 8 fertilizer treatments were randomized among the 24 soil chambers for each soil, thus 3 replication of each fertilizer were present for each of the 4 soils. Ammonia volatilization potential was measured in the glass chambers contained inside customized, environment regulated cabinets (Woodward et al., 2011). The glass chambers had a total volume of 1200 mL and were sealed with air-tight lids. The glass chamber lids were fitted with three air-tight openings. The first was used to attach a thermocouple to monitor soil temperature while the other two were used to attach tubing for an air inlet and outlet.

To initiate the volatility study, the glass chambers were filled with 500 g of air-dried soil sieved through a 2 mm mesh sieve. Deionized water was added to each soil at a moisture content equivalent to 22 kPa soil water suction representing 2/3 field capacity (Table 2.3). This ensured that moisture was adequate and not limiting for ammonia volatilization. The glass chambers were sealed and incubated for 48 h prior to the start of the experiment at a constant temperature of 26°C. Nitrogen fertilizer granules (2 – 2.38 mm) were then surface applied at an equivalent N rate of 135 kg ha<sup>-1</sup> based on the exposed soil surface area within the glass chambers.

To collect ammonia released from fertilizer materials, air was passed through two humistats prior to passing through the volatilization chambers. The air flow was through each chamber was regulated by calibrating individual flow control units which preceded the humistats. The air flow was set to 1 liter per minute which represents a turnover rate of 33 – 35 second.

After passing through the volatilization chambers, the air containing any ammonia gas was captured in 100 ml of 0.02 M orthophosphoric acid. The orthophosphoric acid traps were changed 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, and 14 d after the application of the N fertilizer. Acid traps were weighed prior to and after each sampling time in order to ensure accurate volume correction. Ammonium was measured with an automated QuikChem® 8500 Series 2 flow injection analyzer system by salicylate-hypochlorite method (QuikChem® Method 12-107-06-2-H) (Lachat Instruments, Loveland, CO). Cumulative ammonia volatilized 5, 9, and 14 d after application was reported and discussed in this study. Cumulative ammonia volatilization after 5 d was evaluated since it coincides with the period of rapid ammonia loss. Monitoring ammonia loss during this period provided an opportunity to evaluate the performance of experimental

fertilizers. In delayed-flood rice production, producers on average establish permanent flood within 10 d following preflood N application.

### 2.2.5 Statistical Analysis

Analysis of variance of the SMCC suction data was performed using the PROC MIXED procedure in SAS 9.4 (SAS Institute, 2013). Treatment means were separated using the Tukey multiple comparison test at  $\alpha = 0.05$ . Analysis of variance of the cumulative ammonia volatilized after 5, 9, and 14 d after N fertilization was conducted separately using the PROC MIXED procedure in SAS. Soil and N fertilizer source were considered fixed effects while replication was considered a random effect. Mean separation of significant effects was determined by using orthogonal contrasts analysis at  $\alpha = 0.05$ .

## 2.3 Results and Discussion

### 2.3.1 Soil Moisture Characteristic Curve

A soil's available moisture content has an impact on urea hydrolysis and subsequent ammonia volatilization (Sommer et al., 2004; Lui et al., 2007). The SMCC of the four soils used in this study are presented in Fig. 2.1. The curves were developed to evaluate moisture behavior of the soils and can be a reliable methodology to predict moisture at FC. The van Genuchten equation showed a good fit for the entire range of suction for all four soils ( $R^2 = 0.97 - 0.99$ ). The incremental suction of the Crowley H and Crowley L soils did not encompass abrupt changes in volumetric soil moisture content at low suctions (10 – 100 kPa) and; therefore, the equation is only considered a good predictor of the moisture retention within this range of suction (Hillel, 2004). The shape of SMCC for Crowley L and H soils were similar, and the shape of curve is considered an intermediate between silt and clay soils (Hillel, 2004). Despite the similarities in the shape of the Crowley H and Crowley L curves, the moisture retained at



lower suctions (<100 kPa) for the Crowley H was significantly higher than Crowley L with the exception of the retention at 10 kPa (Table 2.5). Changes in the moisture retention of soils with a similar particle size distribution at low suctions (<100 kPa) are typically explained by changes in soil structure (Hillel, 2004; Tuller and Or, 2003). The Crowley L has been in a rice-fallow rotation for more than two decades, while the Crowley H soil has been in a rice-soybean rotation for a similar time frame. Undisturbed core samples of both soils were taken in the winter of 2015. The Crowley L was in the one-year fallow period when the samples were taken, while the Crowley H soil was following the soybean (*Glycine max*) crop and post-harvest fall tillage. The rotation differences between the two soils may help partially explain the potential soil structure differences predicted by the SMCC of these two soils at low soil suctions (<100 kPa). In addition, the Crowley H soil had a higher soil organic matter content which may further help explain the difference in moisture retention between these two soils (Table 2.1). Changes in the soil moisture retention of soils at high suction (>100 kPa) values are typically explained by changes in soil particle size distribution (Hillel, 2003). The moisture content at high suction (>100 kPa) did not differ between the Crowley L and H soils (Table 2.5). The lack of difference is explained by only the slight differences observed in the soil particle size distribution of the two soils (Table 2.2).

The van Genuchten equation resulted in a good fit ( $R^2 = 0.99$  and  $R^2 = 0.99$  for Kinder and Mowata, respectively) for the moisture retention data of the Kinder and Mowata soils (Fig. 2.1) for the entire suction range. The shape of SMCCs for the Kinder and Mowata soils were more linear at low suction (<100 kPa) values as compared with the Crowley L and Crowley H soils. Their shape did not provide a distinct change in wetness versus suction. Linear van Genuchten models within the low suction range (<100 kPa) are considered to be less reliable

predictors of soil moisture retention as compared to models which are curvilinear within this range. A gradual decrease in wetness was observed for the Mowata and Kinder soils. The difference in shape of Crowley soils compared to Kinder and Mowata soils can be attributed higher sand contents in later soils. The high sand contents suggest that the pore sized in Mowata and Kinder soils may be larger and hence drainage is faster. Nonetheless, the SMCCs imply that FC estimation was not possible to achieve for Mowata and Kinder soils thus moisture content at FC values selected will be arbitrary between 50 – 100 kPa. Therefore, independent FC values determined at 33 kPa were used for the ammonia volatilization experiment (Table 2.2).

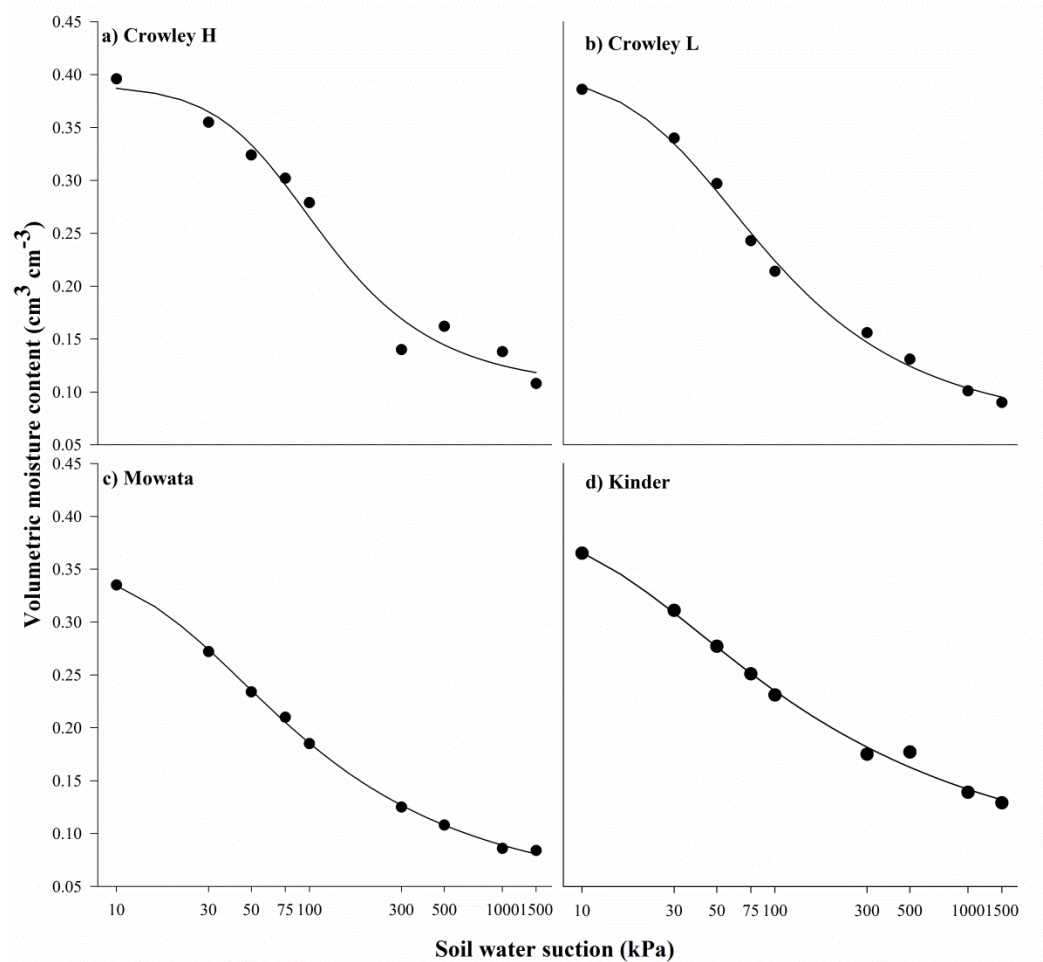


Figure 2.1 Soil moisture characteristic curves for a) Crowley H (pH 7.4), b) Crowley L (pH 6.6), c) Mowata, and d) Kinder silt loam soils at water suction points of 10, 30, 50, 75, 100, 300, 500, 1000, and 1500 kPa.

Table 2.5 Mean volumetric moisture content for Crowley H, Crowley L, Kinder, and Mowata silt loam soils at 10, 30, 50, 75, 100, 300, 500, 1000, and 1500 kPa of soil water suction.

Soil <sup>†</sup>	Soil water suction								
	10	30	50	75	100	300	500	1000	1500
	cm <sup>3</sup> cm <sup>-3</sup>								
Crowley L	0.39 ab	0.34 b	0.30 b	0.24 b	0.21 b	0.16 a	0.13 ab	0.10 ab	0.09 a
Crowley H	0.40 a	0.36 a	0.32 a	0.30 a	0.28 a	0.14 a	0.16 ab	0.14 a	0.11 a
Kinder	0.37 b	0.31 c	0.28 b	0.25 b	0.23 b	0.18 a	0.18 a	0.14 a	0.13 a
Mowata	0.34 c	0.27 d	0.23 c	0.21 c	0.19 c	0.13 a	0.11 b	0.09 b	0.09 a

<sup>†</sup>Crowley L, Crowley silt loam (pH 6.6); Crowley H, Crowley silt loam (pH 7.4).

Means followed by the same letters within each column are not significantly different using Tukey's test *P* (0.05).

### 2.3.2 Ammonia Volatilization

The ANOVA for the main effects of soil and N sources and their interaction are shown in Table 2.6. There was a significant interaction between soil and N fertilizer source for cumulative ammonia volatilization loss after 5, 9, and 14 d following application (Table 2.6). However, the main effects are reported and discussed in order to present results that generate meaningful comparisons. Ammonia volatilization between the N fertilizer sources was evaluated for each soil using orthogonal contrasts. Orthogonal contrasts were preferred over traditional multiple range tests to avoid increasing the chance of a type 2 error. Cumulative ammonia volatilization loss from each N fertilizer source was also compared across soils using orthogonal contrasts.

#### 2.3.2.1 Urea

Cumulative ammonia loss during the first 5 d following urea application is shown in Table 2.7. During this period, ammonia loss from urea on Mowata, Crowley H, Crowley L, and Kinder soils was 5.1, 9.5, 12.7, and 13.9%, respectively. With the exception of Mowata soil, ammonia volatilization from urea during the first 5 d represented 46 – 60% of the total ammonia loss during the 14 d study (Tables 2.7 and 2.9). The high ammonia loss following urea application during the first 5 d is attributed to urea hydrolysis. Urea hydrolysis raised the soil pH around the urea granules and increased the conversion of ammonium to ammonia (Mikkelsen, 2009). Mikkelsen (2009) reported that pH surrounding the urea granules increased from 4.9 to 9 following urea application within the first 3 d which coincided with the highest daily ammonia loss. In this study, the highest daily ammonia loss following urea application was measured 4 d after fertilizer application with the exception of the Mowata soil (Fig. 2.2). The buffering capacity of Mowata soil may have delayed the peak ammonia loss until 6 d after fertilization (Fig. 2.2). Previous studies have shown that urea can volatilize at least 50% of the total ammonia

loss within its first 5 d after application (Rawluk et al., 2001; Norman et al., 2009; Holcomb et al., 2011).

Urea volatilized significantly less ammonia from the Mowata soil as compared to the other soils (Table 2.7). Since soil pH and buffering capacity have a strong effect on ammonia volatilization, the relatively lower ammonia loss on the Mowata soil may be partly attributed to the soil properties. The pH of the Crowley H, Crowley L, Kinder, and Mowata soils was 7.4, 6.6, 6.6, and 5.8, respectively (Table 2.1). Acidic soils can neutralize  $\text{OH}^-$  ions produced during urea hydrolysis. Therefore, urea hydrolysis in the Mowata soil may not have significantly elevated the soil pH around each granule to promote a high rate of ammonia volatilization (Fenn and Hossner, 1985; Reddy and Sharma, 2000). Furthermore, acidic soils favor the protonation of ammonia into ammonium thus suppressing ammonia volatilization. Soil properties that influence buffering capacity, such as cation exchange capacity (CEC) and organic matter (OM) (Table 2.1) were either lower or comparable to the other soils except for the clay content of the Mowata soil (Table 2.2). The high clay content may have temporarily delayed a rapid increase in soil pH during the first 5 d. Cumulative ammonia loss from Crowley H was significantly lower than the Crowley L and Kinder soils despite having the highest soil pH (Table 2.7). This can be partially explained by CEC which was approximately 2 times higher compared to the other soils (Table 2.1). The higher CEC likely increased ammonium retention and decreased ammonium concentration in soil solution, thus reducing the potential for ammonia volatilization (Jones et al., 2007; Reddy and DeLaune, 2008). According to Keller and Mengel (1986) ammonia volatilization from a soil with a CEC of  $7 \text{ cmol}_c \text{ kg}^{-1}$  following urea application was about 3 times greater than the soil with a CEC of  $12 \text{ cmol}_c \text{ kg}^{-1}$ . The higher OM content of Crowley H may have also contributed to suppressing ammonia volatilization (Francis et al., 2008). In

addition, the high levels of exchangeable Ca in the Crowley H soil may have counteracted the pH increase produced by urea hydrolysis.

Cumulative ammonia loss after 9 d following urea application on the Mowata, Crowley H, Crowley L, and Kinder soils were 11.8, 14.2, 21.9 and 22.5%, respectively. Ammonia loss during the first 5 d increased by 49, 62, 72, and 130% over the next 4 d in Crowley H, Kinder, Crowley L, and Mowata soils, respectively (Table 2.8). Cumulative ammonia loss on Mowata soil following urea application was statistically similar to Crowley H soil but lower than Crowley L and Kinder soils. The reason for the difference in ammonia volatility between soils is similar to what was reported for the first 5 d. Cumulative ammonia loss after d 9 following urea application represented 80 – 92% of total ammonia loss by the end of the study (Table 2.8). The results from the current study shows that the time between urea application and the first 9 d prior to flooding is very important, particularly for poorly buffered soils. Up to 23% of the available N supplied by urea can be lost as ammonia when flooding is delayed until 9 d following application.

A decline in the daily ammonia volatilization rate of urea was observed after d 9 for all soils (Fig. 2.2). In Crowley H and Mowata soils, cumulative ammonia loss from urea leveled off 11 d after N fertilization (Fig. 2.3). However, in Crowley L and Kinder soils, ammonia volatilization proceeded until the end of the study. The low ammonium concentration in soil solution and the decline in soil pH from  $H^+$  ions potentially produced during nitrification may have decreased ammonia volatility (Francis et al., 2008). Cumulative ammonia loss from urea at the end of study for Mowata, Crowley H, Kinder, and Crowley L soils fertilized with urea was 14, 15.5, 25.8, and 27.5%, respectively (Fig. 2.2; Table 2.9). Cumulative ammonia loss on the

Mowata soil following urea application was statistically similar to Crowley H soil but lower than Crowley L and Kinder soils.

#### 2.3.2.2 Urea Treated with NBPT

The inhibitory effect of NBPT on ammonia volatilization loss from urea was evaluated at three application rates; 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT. Cumulative ammonia volatilization after 5 d from 0.3, 0.6 and 0.9 g kg<sup>-1</sup> NBPT-treated urea for all soils is presented in Table 2.7. Urea treated with NBPT effectively suppressed ammonia volatilization on all soils during the first 5 d. Only 0.3 – 4.1% of the NBPT-treated urea applied on soil surface had volatilized during the first 5 d compared to 5.1 – 13.9% from urea (Table 2.7). Similarly, Norman et al. (2009) reported that the cumulative ammonia loss after 5 d from 0.8 g kg<sup>-1</sup> NBPT-treated urea ranged from 1.7 – 2.2%. The treatment of urea with NBPT has been reported to slow urea hydrolysis and, thus, temporarily avoided rapid increase in soil pH which serves as a catalyst for increased ammonia volatilization. Slow urea hydrolysis also reduces the availability of ammonium to convert into ammonia (Jones et al., 2007). NBPT inhibits urea hydrolysis due to its similar fit in the binding site of the urease enzyme which temporary halts the ability of urease to attack urea and promote urea hydrolysis (Amtul et al., 2002).

Ammonia volatilization was slightly higher for urea treated with 0.3 g kg<sup>-1</sup> NBPT (1.2 – 4.1%) than urea treated with 0.6 (0.5 – 2.0%) and 0.9 g kg<sup>-1</sup> NBPT (0.3 – 1.8%); however, the difference was not statistically significant (Table 2.7). Generally, an increase in inhibitory effect is expected with increasing NBPT application rates (Rawluk et al., 2001). Urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT reduced cumulative ammonia volatilization during the first 5 d by 57 – 89, 81 – 91, and 81 – 94%, respectively (Table 2.7). During the first 5 d, ammonia volatilization from 0.3 g kg<sup>-1</sup> NBPT-treated urea was statistically similar between the Crowley H, Crowley L

and Kinder soils; however, ammonia volatilization was significantly higher for the Crowley H soil as compared to the Mowata soil (Table 2.7). Cumulative ammonia volatilization from the 0.6 and 0.9 g kg<sup>-1</sup> NBPT treated urea was not significantly different among the four soils despite small differences in the cumulative amount of ammonia volatilized. This suggests that soil properties may not influence the performance of NBPT during the first 5 d after application for rates of NBPT at 0.6 – 0.9 g kg<sup>-1</sup>; however, rates of 0.3 g kg<sup>-1</sup> may not be sufficient to suppress volatilization for some soils.

Cumulative ammonia volatilization from 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT-treated urea on experimental soils 9 d after fertilization is shown in Table 2.8. Cumulative ammonia volatilization during the first 9 d from 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT-treated urea across soils were 6.0 – 7.2, 4.3 – 9.0, and 3.5 – 7.0%, respectively. Cumulative ammonia loss from all rates of NBPT-treated urea between 5 and 9 d was higher than the first 5 d after fertilization. This occurred because the addition of NBPT delayed urea hydrolysis and subsequently ammonia volatilization until 6 d after fertilizer application as shown in Fig. 2. Urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT to the urea reduced ammonia loss by 39 – 72, 60 – 74, and 68 – 77%, respectively, across all soils. The range of loss reported in this study was within the range reported previously (Dillon et al., 2012; Norman et al., 2009). A significant difference in ammonia volatilization loss between rates of NBPT-treated urea during the time period between 5 and 9 d after application was only evident when the N was applied on the Mowata soil. When applied onto the Mowata soil, the loss from the 0.3 g kg<sup>-1</sup> (7.1%) was higher than the 0.9 g kg<sup>-1</sup> NBPT-treated urea (3.5%). Cumulative N loss was statistically similar 9 d after application of the 0.3 g kg<sup>-1</sup> NBPT-treated urea on all four soils. In contrast, the loss from 0.6, and 0.9 g kg<sup>-1</sup> of NBPT-treated urea during the same period was significantly different between soils. The



ammonia volatilized from the 0.9 g kg<sup>-1</sup> NBPT-treated urea 9 d after application on the Mowata soil was comparable to the Crowley H but was lower than the Kinder and Crowley L soils. There was no significant difference between Crowley H, Crowley L, and Kinder soils. Studies have reported that ammonia volatilization from NBPT-treated urea is dependent on soil properties (Rawluk et al., 2001; Cantarella et al., 2008). Generally, ammonia volatilization was lower on soils with lower ammonia volatilization potential from urea. The daily ammonia loss for all rates of NBPT-treated urea fertilizers 9 d after application was similar or higher than urea indicating that the inhibitory effect of modified fertilizers declined gradually (Fig. 2). The decrease in efficiency can be attributed to degradation of NBPT or displacement of NBPT by urea at the urease enzyme active site (Jones et al., 2013).

Cumulative ammonia volatilization loss for all rates of NBPT treated urea 14 d after fertilization is shown in Fig. 2 and Table 2.9. The total ammonia loss from 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT-treated urea across soils was 8.5 – 11.4, 5.6 – 13.4, and 5.7 – 11.5%, respectively. During the 14 d study, 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT added to urea reduced ammonia loss by 27 – 60, 37 – 64, and 40 – 63%, respectively, across all soils. The addition of NBPT significantly reduced ammonia loss from all soils; however, its effect was minimal in the Mowata soil. Cumulative ammonia loss was not different between all NBPT rates for each soil apart from the Kinder soil, where the loss from 0.3 was higher than 0.9 g kg<sup>-1</sup> NBPT. Cumulative N loss 14 d after application of the 0.3g kg<sup>-1</sup> NBPT-treated urea was statistically similar between the four soils. However, the total cumulative volatilization loss from the 0.6 and 0.9 g kg<sup>-1</sup> NBPT-treated urea during the same period was significantly lower for the Crowley H soil as compared to the Crowley L and Kinder soils. In cases where flooding cannot be established in a timely manner, a urease inhibitor should be used to reduce the potential of N losses from ammonia volatilization.

### 2.3.2.3 Physical Coating Only (RCO3)

Ammonia volatilization potential was evaluated for four experimental zinc sulfate coated urea (ZSCU) fertilizers; RCO3, RCO5, RCO4, and RCO4S. The RCO3 fertilizer was manufactured by physically coating urea granules with zinc sulfate. The cumulative ammonia volatilization 5 d after fertilization for RCO3 is shown in Table 2.7. During the first 5 d after fertilization, RCO3 volatilized 1.3, 5.5, 7.5, and 8.3% of total N applied on Mowata, Crowley L, Kinder, and Crowley H soils, respectively. During this time, RCO3 reduced ammonia volatilization by 41 – 89% across four soils as compared to urea. The reduction in the amount of ammonia volatilized from RCO3 as compared to urea contradicts previous findings by Hawke and Baldock (2010). The authors reported that there was no evidence that zinc sulfate coated urea (10 g Zn kg<sup>-1</sup>) reduced ammonia volatilization during the 7 d trial. The ZSCU used in the current study (20 g kg<sup>-1</sup>) may have been relatively thicker than those used in the previous study (10 g Zn kg<sup>-1</sup>) since twice as much Zn was added to urea. Physical coatings decrease the urea surface area for urease attack, thus slow down urea hydrolysis and subsequently minimize the rate of ammonia volatilization. The zinc coating of RCO3 was less effective than NBPT in reducing volatile N losses during the first 5 d (Table 2.7); however, there was some delay in volatile N losses for all soils except Crowley H (Fig. 2). We believe that this is due to the higher pH of the Crowley H soil. All the rates of NBPT-treated urea 5 d after application reduced volatilization as compared to RCO3 across soils with the exception of the Mowata soil (Table 2.7). This suggests that a physical coating of a single metal ion alone will not be as effective as NBPT on soils with a high volatilization potential in the first 5 d after fertilizer application. The amount of ammonia volatilized 9 d after fertilization for RCO3 applied on the Mowata, Crowley H, Kinder, and Crowley L soils was 7.4, 12.4, 14.2, and 15.1%, respectively. Cumulative

ammonia losses from RCO3 during this period were greater for the Crowley L, Kinder, and Crowley H soils as compared to the Mowata soil. RCO3 volatilized more ammonia than all rates of NBPT-treated urea across soils with the exception of the Mowata soil.

Cumulative ammonia volatilization loss from RCO3 14 d after fertilization is shown in Fig. 2 and Table 2.9. Cumulative ammonia volatilization for RCO3 14 d after fertilization was between 9.9 – 20.8% across soils (Table 2.9). During this period, ammonia loss from RCO3 applied on the Mowata soil (9.9%) was significantly similar to Crowley H (13.4%) but lower than Crowley L (20.8%) and Kinder (16.8%) soils (Table 2.9). The differences in volatilization potential suggest that the effectiveness of ZSCU to reduce ammonia volatilization is highly dependent on soil properties unlike NBPT which has shown to be efficient over a wide range of soil types. Reduction in ammonia loss of 14 to 35% over urea was observed for RCO3 14 d after application which is similar to what has been reported for sulfur,  $K_2SO_4$ , and  $CaSO_4$  coated urea (Prasad 1976; Knight et al. 2007; Frame et al., 2012). The lower volatilization loss associated with RCO3 can be attributed to the slower hydrolysis of urea due to the physical coating. Physically coating the urea alone did not significantly decrease cumulative ammonia volatilization loss beyond what was observed from 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT in Crowley H, Crowley L, and Kinder soil.

#### 2.3.2.4 Physical Coating plus Boron (RCO5)

The RCO5 experimental ZSCU contained 1.7 g B kg<sup>-1</sup> in the binder that was used to attach the zinc sulfate to the surface of the urea granules. Surface broadcast of RCO5 significantly reduced cumulative ammonia volatilization losses 5 d after application as compared to urea across all soils (Table 2.7). The highest cumulative ammonia volatilization loss 5 d after fertilization occurred on the Crowley H soil (6.0%), which was significantly higher than the

Mowata (0.8%) and Crowley L (2.1%) soils but was statistically similar to the Kinder (3.4%) soil. RCO5 significantly decreased the ammonia volatilized by 36 – 84% as compared to urea over the first 5 d after application. Cumulative ammonia volatilization losses from RCO5 5 d after fertilization was statistically similar to urea treated with NBPT at rates of 0.3, 0.6, and 0.9 g kg<sup>-1</sup> on the Crowley L, Kinder, and Mowata soils. RCO5 significantly reduced ammonia volatilization as compared to RCO3 on the Crowley L and Kinder soils. This difference in volatilization control between RCO3 and RCO5 suggests that the addition of B in the binding agent, which was used in making RCO5 and not used in RCO3, provided the improved volatilization control. Similarly, Pursell et al. (2014) found that ammonia volatilization from urea during a 10 d trial was 3.6 times greater than urea coated with 5% boric acid using a corn syrup binder. RCO5 had statistically similar ammonia volatilization losses as RCO3 5 d after N application on the Crowley H and Mowata soils (Table 2.7). This suggests that the physical zinc sulfate coating alone was sufficient to minimize ammonia volatility in these soils which have a lower ammonia volatilization loss potential. In general, the addition of B to the binding agent used in creating RCO5 was more effective in reducing ammonia volatilization as compared to RCO3, which only has the zinc sulfate coating alone, on soils that are highly susceptible to ammonia volatilization during the first 5 d after application.

RCO5 volatilized 3.8, 7.2, 8.0, and 9.6% of total N applied 9 d after fertilization on the Mowata, Crowley L, Kinder, and Crowley H soils, respectively (Table 2.8). During this period, ammonia loss from RCO5 applied on Mowata was significantly lower compared to the other soils. RCO5 reduced cumulative ammonia loss 9 d after fertilizer application by 32 – 68% as compared to urea across all four soils. Cumulative ammonia loss from RCO5 during this period was statistically comparable to urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT applied on the

Crowley L, Kinder, and Mowata soils. However, cumulative volatilization losses of RCO5 were higher on the Crowley H soil when compared to urea treated with 0.6 and 0.9 g kg<sup>-1</sup> NBPT. The Crowley H soil (pH 7.4) has the highest pH of all the soils evaluated in this experiment which suggests that the effectiveness of RCO5 to reduce ammonia volatilization may be reduced on more alkaline soils. The cumulative ammonia loss from RCO5 9 d after application was similar to RCO3 for soils with lower ammonia volatilization potential (Crowley H and Mowata) but less on soils with higher ammonia volatilization potential (Crowley L and Kinder).

Cumulative ammonia volatilization for RCO5 14 d after application ranged between 6.3 and 12.6% across soils (Table 2.9). During this period, ammonia loss from RCO5 applied to the Mowata soil (6.3%) was significantly similar to Crowley H (10.7%) and Kinder (10.8%) soils but lower than Crowley L (12.6%) soil (Table 2.9). Accordingly, reduction in ammonia loss of 30 to 58% over urea was observed when RCO5 was applied during the 14-d study. While the cumulative ammonia loss from RCO5 was statistically similar to RCO3 on soils with lower ammonia loss, RCO5 volatilized less ammonia than RCO3 on soils with higher ammonia loss. Cumulative ammonia volatilized from RCO5 during this period was statistically comparable to all rates of NBPT-treated urea apart from the loss from Crowley H soil.

#### 2.3.2.5 Physical Coating plus NBPT (RCO4)

RCO4 was prepared by first treating the urea with 0.6 g kg<sup>-1</sup> NBPT and then coating it with zinc sulfate using a binder containing 1.7 g B kg<sup>-1</sup>. Cumulative ammonia loss from RCO4 within the first 5 d following application on all soils is shown in Table 2.7. Ammonia loss from RCO4 over this period on the Kinder soil (4.6%) was significantly higher as compared to the Mowata (0.5%) and Crowley L (1.5%) soils but similar to the Crowley H (2.8%) soil. RCO4 reduced ammonia volatilization by 67 – 90% 5 d after application as compared to urea across all

soils. Ammonia volatilization from RCO4 was statistically similar to urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT across all soils. Ammonia loss from RCO4 was similar to RCO5 when applied on the Crowley L, Kinder, and Mowata soils. However, for the higher pH Crowley H soil, RCO4 improved volatility control as compared to RCO5. This suggests that the addition of NBPT along with the zinc sulfate coating improved the ability to reduce the N loss compared to the zinc sulfate coated product RCO3 which lacked NBPT.

Cumulative ammonia volatilization 9 d after RCO4 application was 2.6, 4.7, 5.3, and 9.3% for the Mowata, Crowley H, Crowley L, and Kinder soils, respectively. Cumulative ammonia loss from RCO4 9 d after fertilization of the Kinder soil was significantly higher as compared to the other soils (Table 2.8). During this period, RCO4 reduced ammonia volatilization by 58 – 78% as compared to urea across four soils. Ammonia volatilization 9 d after RCO4 application was statistically similar to urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT across all soils. RCO4 reduced ammonia volatilization 9 d after application on the Crowley L and Crowley H soils compared to RCO5, but was statistically similar on the Mowata and Kinder soils.

The highest cumulative ammonia loss from RCO4 14 d after application occurred on the Kinder soil (11.5%), which was significantly higher than the Mowata (4.4%) and Crowley H (5.3%) soils but statistically similar to Crowley L (8.7%) soil. The cumulative ammonia loss from ZSCU in combination with NBPT (4.4 – 11.5%) was lower than that reported previously using nutrient-coated urea fertilizers in combination with NBPT (Frame et al., 2012). According to Frame et al. (2012), the cumulative ammonia volatilization from K<sub>2</sub>SO<sub>4</sub> and CaSO<sub>4</sub> coated urea in combination with NBPT 14 d after application ranged from 17.9 to 24.8%. RCO4 reduced cumulative ammonia loss by 49 – 63% when compared to urea across all soils during the

14 d trial (Table 2.9). Cumulative ammonia volatilization from RCO4 was statistically similar to urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT across all soils. Cumulative ammonia losses of RCO4 (which contained NBPT, B, and the zinc sulfate coating) were significantly lower than cumulative ammonia of RCO3 (which only contained the zinc sulfate coating) across all soils during the 14 d trial. The addition of NBPT to urea prior to coating with zinc sulfate as was done for RCO4 significantly decreased cumulative ammonia losses by 5.4% 14d after application when applied on the Crowley H soil as compared to RCO5 which did not have NBPT (Table 2.8). Cumulative ammonia losses 14 d after application for RCO4 and RCO5 were not different when applied on the other soils in this study. This suggests that the benefit of the addition of NBPT to the physical coating with zinc sulfate and boron was only needed on Crowley H which was the most aggressive in terms of volatile n losses due to its high pH.

#### 2.3.2.6 Physical Coating plus NBPT and Calcium sulfate Coating (RCO4S)

RCO4S was similar to RCO4 except that it contained an additional coating of calcium sulfate after the NBPT was treated on the urea and prior to the addition of the zinc sulfate coating (Table 2.4). Urea coated with CaSO<sub>4</sub> has been reported to reduce ammonia volatilization (Frame et al., 2012). Cumulative ammonia volatilization over the first 5 d after RCO4S application is presented in Table 2.7. During this period, RCO4S volatilized 0.4, 1.0, 3.3, and 3.7% of the total N applied on the Mowata, Crowley L, Kinder, and Crowley H soils, respectively. Cumulative ammonia loss on the Mowata soil following RCO4S application was significantly lower than the other soils except the Crowley L soil (Table 2.7). RCO4S reduced ammonia volatilization by 61 – 92% across all four soils 5 d after application. Cumulative ammonia volatilization from RCO4S was similar to urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT across all soils. The cumulative ammonia volatilization after 9 d following RCO4S application is shown in Table 2.8.

Cumulative ammonia volatilization from RCO4S 9 d after application on the Kinder (8.6%) was significantly higher than the Mowata (1.6%), Crowley L (3.6%), and Crowley H (5.7%) soils. During this time, RCO4S reduced ammonia volatilization by 60 – 86% relative to urea across all four soils. Cumulative ammonia volatilization from RCO4S was statistically similar to urea treated with 0.3, 0.6, and 0.9 g kg<sup>-1</sup> NBPT across soils with the exception of the Mowata soil. Ammonia volatilization from RCO4S during the first 9 d after application on the Mowata soil was not significantly different from urea treated 0.6 and 0.9 g kg<sup>-1</sup> NBPT but was significantly lower than urea treated with 0.3 g kg<sup>-1</sup> NBPT. Ammonia volatilization from RCO4S was similar to RCO5 and RCO4 across all four soils.

Cumulative ammonia volatilization loss 14 d after RCO4S application is shown in Table 2.9. Cumulative ammonia volatilization after 14 d following RCO4S application on the Mowata, Crowley H, Crowley L, and Kinder soils was 2.6, 6.4, 7.2, and 11.6%, respectively. Cumulative ammonia loss from RCO4S 14 d after application on the Mowata soil was statistically similar to the Crowley H and Crowley L soils, but was significantly lower as compared to the Kinder soil. However, the loss on the Kinder soil was significantly similar to Crowley L soil. RCO4S reduced ammonia volatilization by 55 – 81% 14 d after application across all four soils. Ammonia loss from RCO4S was statistically similar to urea treated with 0.3, 0.6 and 0.9 g kg<sup>-1</sup> NBPT across all soils with the exception of the Mowata soil. Cumulative ammonia volatilization from RCO4S was significantly lower than urea treated with 0.3 g kg<sup>-1</sup> NBPT. Ammonia volatilization from RCO4S was similar to RCO5 and RCO4 across all soils.



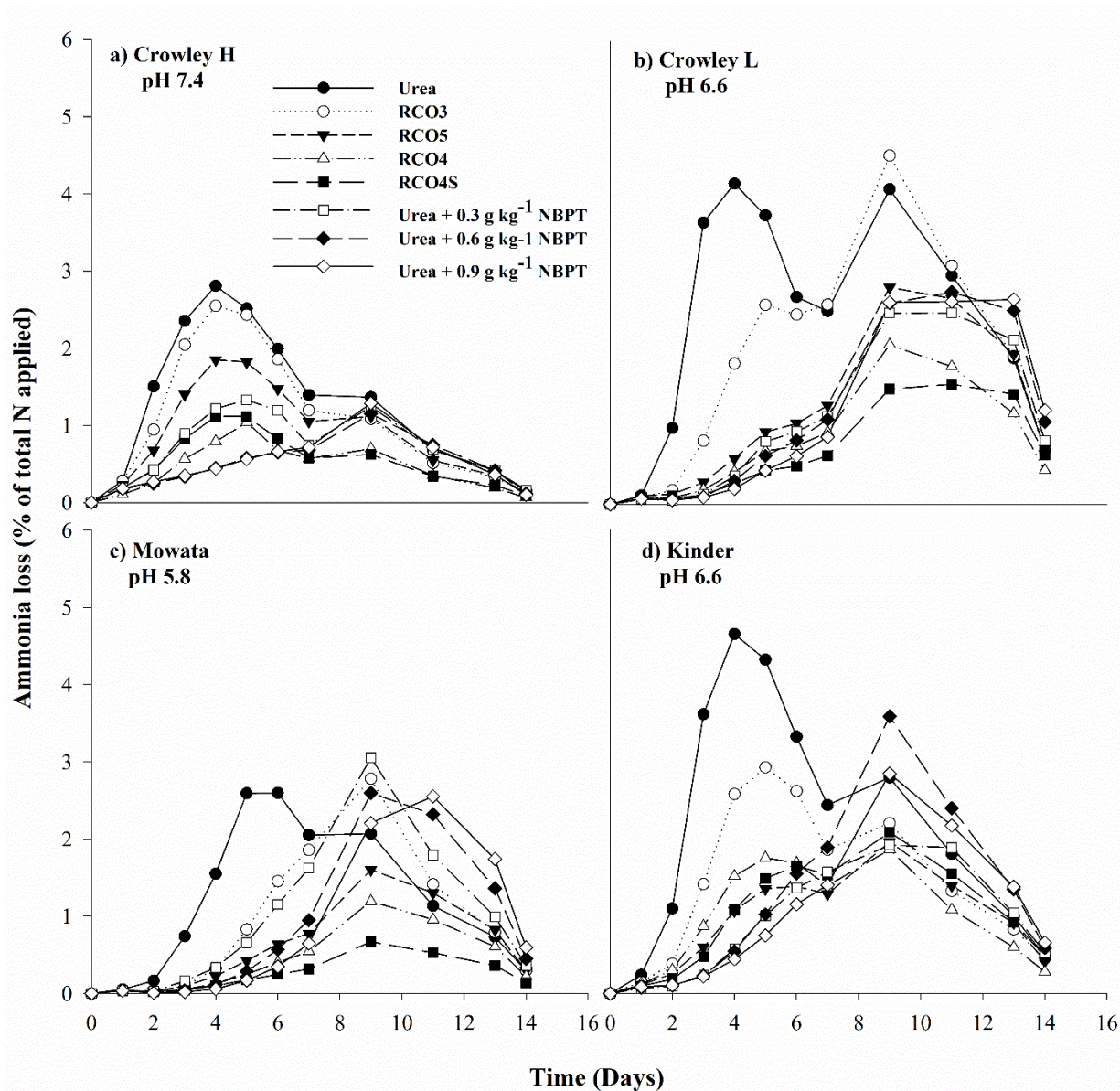


Figure 2.2 Mean daily ammonia loss from urea, urea treated with NBPT, and experimental zinc sulfate coated urea (ZSCU) fertilizers for 14 d after application on a) Crowley H, b) Crowley L, c) Mowata, and d) Kinder silt loam soils.

RCO3, ZSCU only; RCO4, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT; RCO4S, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT + CaSO<sub>4</sub> coating; RCO5, ZSCU + 1.7 g B kg<sup>-1</sup>.

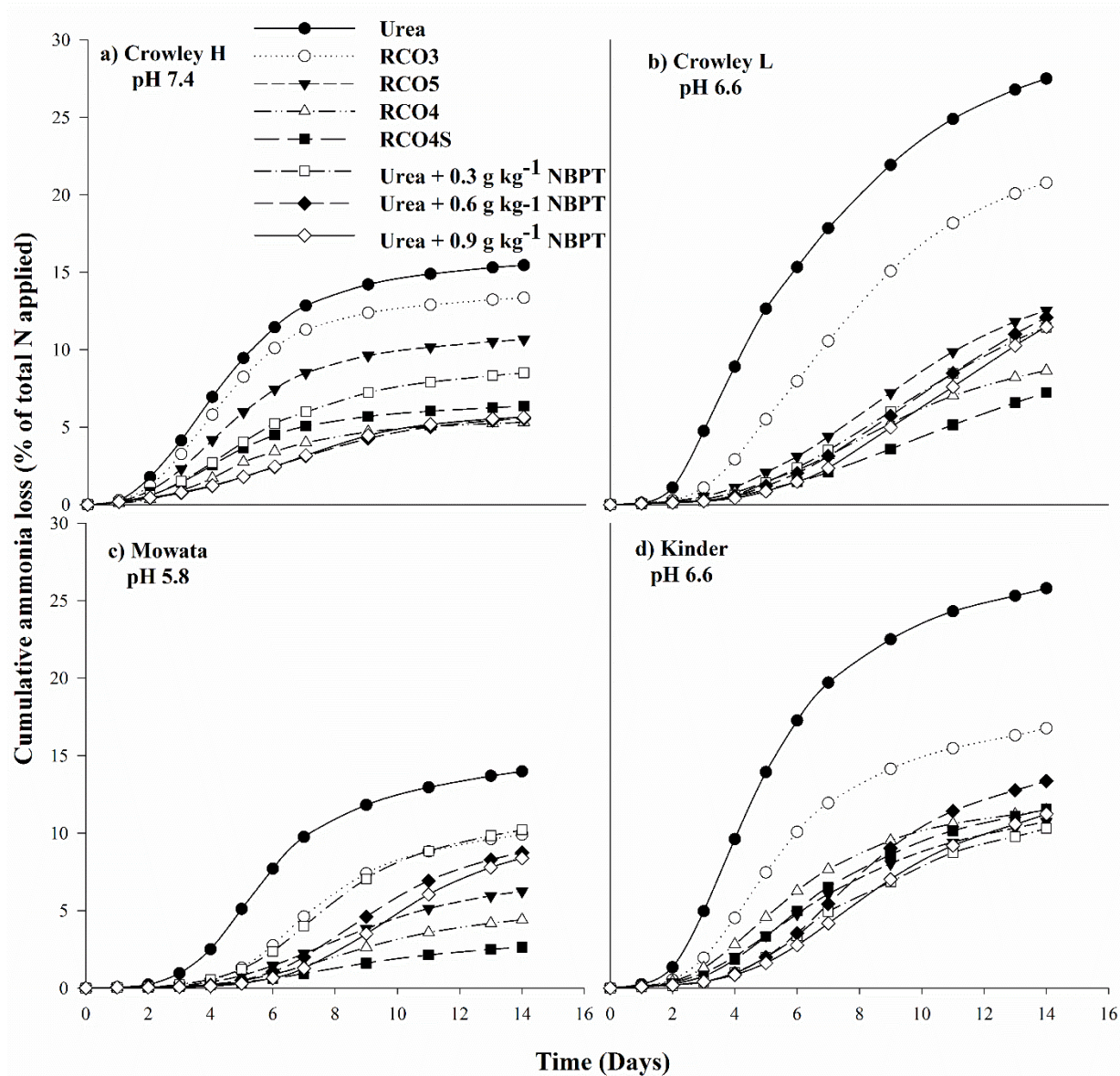


Figure 2.3 Mean cumulative N loss from urea, urea treated with NBPT, and experimental zinc sulfate coated urea (ZSCU) fertilizers for 14 d after application on a) Crowley H, b) Crowley L, c) Mowata, and d) Kinder silt loam soils. RCO3, ZSCU only; RCO4, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT; RCO4S, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT+ CaSO<sub>4</sub> coating; RCO5, ZSCU + 1.7 g B kg<sup>-1</sup>.

Table 2.6 Analysis of variance for cumulative N loss after 5, 9, and 14 d after N fertilization.

Source of variation	5	9	14
Soil	<.0001	<.0001	<.0001
Nitrogen Source	<.0001	<.0001	<.0001
Soil x Nitrogen Source	0.0010	0.0041	0.0121

Table 2.7 Cumulative N loss after 5 d after application from urea, N-(n-Butyl) thiophosphoric triamide (NBPT) treat urea, and zinc sulfate coated urea (ZSCU) fertilizers (RCO3, RCO4, RCO4S, and RCO5) applied on Crowley H, Crowley L, Kinder, and Mowata silt loam soils.

Nitrogen Source <sup>†</sup>	Cumulative N loss (5 d after application)			
	Crowley L <sup>‡</sup>	Crowley H <sup>§</sup>	Kinder	Mowata
	-----%-----			
Urea	12.7 a (a)	9.5 a (b)	13.9 a (a)	5.1 a (c)
Urea + 0.3 g kg <sup>-1</sup> NBPT	1.4 c (ab)	4.1 cd (a)	2.0 cd (ab)	1.2 b (b)
Urea + 0.6 g kg <sup>-1</sup> NBPT	1.2 c (a)	1.8 d (a)	2.0 cd (a)	0.5 b (a)
Urea + 0.9 g kg <sup>-1</sup> NBPT	0.9 c (a)	1.8 d (a)	1.6 d (a)	0.3 b (a)
RCO3	5.5 b (b)	8.3 ab (a)	7.5 b (ab)	1.3 b (c)
RCO4	1.5 c (b)	2.8 d (ab)	4.6 c (a)	0.5 b (b)
RCO4S	1.0 c (b)	3.7 cd (a)	3.3 cd (a)	0.4 b (b)
RCO5	2.1 c (b)	6.0 bc (a)	3.4 cd (ab)	0.8 b (b)

<sup>†</sup>NBPT, N-(n-butyl) thiophosphoric triamide; ZSCU, Zinc sulfated coated urea; RCO3, ZSCU only; RCO4, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT; RCO4S, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT+ CaSO<sub>4</sub> coating; RCO5, ZSCU + 1.7 g B kg<sup>-1</sup>.

<sup>‡</sup>Crowley L, Crowley silt loam (pH 6.6).

<sup>§</sup>Crowley H, Crowley silt loam (pH 7.4).

Means followed by the same letter within each column are not statistically different.

Means followed by the same letter in parenthesis within each row are not statistically different.

Table 2.8 Cumulative N loss after 9 d after application from urea, N-(n-Butyl) thiophosphoric triamide (NBPT) treat urea, and zinc sulfate coated urea (ZSCU) fertilizers (RCO3, RCO4, RCO4S, and RCO5) applied on Crowley H, Crowley L, Kinder, and Mowata silt loam soils.

Nitrogen Source <sup>†</sup>	Cumulative N loss (9 d after application)			
	Crowley L <sup>‡</sup>	Crowley H <sup>§</sup>	Kinder	Mowata
	-----%-----			
Urea	21.9 a (a)	14.2 a (b)	22.5 a (a)	11.8 a (b)
Urea + 0.3 g kg <sup>-1</sup> NBPT	6.0 c (a)	7.2 cd (a)	6.9 c (a)	7.1 b (a)
Urea + 0.6 g kg <sup>-1</sup> NBPT	5.8 c (ab)	4.3 d (b)	9.0 c (a)	4.6 bc (b)
Urea + 0.9 g kg <sup>-1</sup> NBPT	5.0 c (a)	4.5 d (ab)	7.0 c (a)	3.5 c (b)
RCO3	15.1 b (a)	12.4 ab (a)	14.2 b (a)	7.4 b (b)
RCO4	5.3 c (b)	4.7 d (b)	9.5 c (a)	2.6 c (b)
RCO4S	3.6 c (bc)	5.7 d (ab)	8.6 c (a)	1.6 c (c)
RCO5	7.2 c (a)	9.6 bc (a)	8.0 c (a)	3.8 bc (b)

<sup>†</sup>NBPT, N-(n-butyl) thiophosphoric triamide; RCO3, ZSCU only; RCO4, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT; RCO4S, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT+ CaSO<sub>4</sub> coating; RCO5, ZSCU + 1.7 g B kg<sup>-1</sup>.

<sup>‡</sup>Crowley L, Crowley silt loam (pH 6.6).

<sup>§</sup>Crowley H, Crowley silt loam (pH 7.4).

Means followed by the same letter within each column are not statistically different.

Means followed by the same letter in parenthesis within each row are not statistically different.

Table 2.9 Cumulative N loss 14 d after application from urea, N-(n-Butyl) thiophosphoric triamide (NBPT) treat urea, and zinc sulfate coated urea (ZSCU) fertilizers (RCO3, RCO4, RCO4S, and RCO5) applied on Crowley H, Crowley L, Kinder, and Mowata silt loam soils.

Nitrogen Source <sup>†</sup>	Cumulative N loss (14 d after application)			
	Crowley L <sup>‡</sup>	Crowley H <sup>§</sup>	Kinder	Mowata
	-----%-----			
Urea	27.5 a (a)	15.5 a (b)	25.8 a (a)	14.0 a (b)
Urea + 0.3 g kg <sup>-1</sup> NBPT	11.4 cd (a)	8.5 cd (a)	10.3 c (a)	10.2 ab (a)
Urea + 0.6 g kg <sup>-1</sup> NBPT	12.1 c (a)	5.6 d (b)	13.4 bc (a)	8.7 bc (ab)
Urea + 0.9 g kg <sup>-1</sup> NBPT	11.5 cd (a)	5.7 d (b)	11.2 c (a)	8.4 bc (ab)
RCO3	20.8 b (a)	13.4 ab (bc)	16.8 b (b)	9.9 ab (c)
RCO4	8.7 cd (ab)	5.3 d (b)	11.5 c (a)	4.4 cd (b)
RCO4S	7.2 d (ab)	6.4 cd (b)	11.6 c (a)	2.6 d (b)
RCO5	12.6 c (a)	10.7 bc (ab)	10.8 c (ab)	6.3 bcd (b)

<sup>†</sup>NBPT, N-(n-butyl) thiophosphoric triamide; RCO3, ZSCU only; RCO4, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT; RCO4S, ZSCU + 1.7 g B kg<sup>-1</sup> + 0.6 g kg<sup>-1</sup> NBPT+ CaSO<sub>4</sub> coating; RCO5, ZSCU + 1.7 g B kg<sup>-1</sup>.

<sup>‡</sup>Crowley L, Crowley silt loam (pH 6.6).

<sup>§</sup>Crowley H, Crowley silt loam (pH 7.4).

Means followed by the same letters within each column are not significantly different.

Means followed by the same letter in parenthesis within each row are not statistically different.

## 2.4 Conclusions

Soil properties and N fertilizer source influenced ammonia volatilization losses during the 14 d study. Cumulative ammonia volatilization from urea (14 – 27.5%) during the 14 d trial was different across soils which supports results from previous studies that soil properties partly governs the rate of ammonia volatilization from N fertilizer sources. In the present study, cumulative ammonia volatilization from urea 14 d after application was lower on the Mowata and Crowley soils which had the lowest soil pH and highest CEC, respectively. The 0.3 and 0.6 g kg<sup>-1</sup> NBPT rate provided statistically similar ammonia volatilization control 14 d after application across all soils as compared to the 0.9 g kg<sup>-1</sup> NBPT rate. Physically coating urea with zinc sulfate reduced cumulative ammonia volatilization across soils; however, its inhibitory

effect on ammonia volatilization was most effective on soils which had potential for greater losses through ammonia volatilization. Volatilization losses from zinc sulfate coated urea (ZSCU) was lower than losses observed from urea treated with  $0.3 \text{ g kg}^{-1}$  NBPT in three of the four soils. The addition of B to the zinc sulfate coating improved the ammonia volatilization control as compared to the zinc sulfate coating alone. The addition of B to the ZSCU also had similar volatilization losses as compared to urea treated with  $0.9 \text{ g kg}^{-1}$  NBPT on three of the four soils. The most effective ZSCU fertilizers in controlling ammonia volatilization were those that also contained  $0.6 \text{ g kg}^{-1}$  NBPT. The addition of a  $\text{CaSO}_4$  coating in addition to the zinc sulfate coating on urea provided similar volatility control as ZSCU with NBPT and B. Zinc sulfate coated urea fertilizers may be beneficial to reduce ammonia volatilization while providing Zn in deficient soils.

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## **Chapter 3. Yield, Nitrogen Use Efficiency (NUE), and Ammonia Volatility of Experimental Zinc Sulfate Coated Urea in Drill-seeded Delayed Flood Rice Production**

### **3.1 Introduction**

Rice (*Oryza sativa*) production in the mid-southern United States relies heavily on nitrogen (N) fertilization for optimal grain yield (Norman et al., 2009; Rogers et al., 2015). Urea is the most commonly used preflood N fertilizer because of its economic advantage in comparison to other N fertilizers sources (Griggs et al., 2007; Dillion et al., 2012). Urea is surface broadcast at the 4- to 5-leaf stage of rice development followed by the establishment of a permanent flood within 10 d for most commercial fields (Harrell et al., 2015). Surface applied urea is hydrolyzed by the urease enzyme into ammonium ( $\text{NH}_4^+$ ) and bicarbonate ( $\text{HCO}_3^-$ ) under favorable environmental conditions within the first 3 d after application (Kissel et al., 1988; Kissel et al., 2008; Jones et al., 2013). Ammonium is then taken up by plants, retained on soil surface, remained in soil solution, or converted into ammonia (Francis et al., 2008). Urea hydrolysis increases soil pH around the urea fertilizer granule which serves as a catalyst for the conversion of  $\text{NH}_4^+$  to ammonia. Surface broadcast urea has a greater potential for ammonia volatilization compared to other N fertilizer sources (Harrell et al., 2015). Studies in the mid-southern United States have shown that when urea is surface broadcast, 20 – 80% of total N applied can be loss through ammonia volatilization (Sommer et al. 2004; Griggs et al., 2007; Francis et al., 2008; Norman et al., 2009; Dillion et al., 2012; Frame et al., 2012; Behera et al., 2013). Substantial ammonia volatilization losses from surface broadcast urea fertilization occur within the first two weeks after application (Jones et al., 2013). Excessive ammonia volatilization losses can cause economic and environmental losses (Francis et al., 2008; Behera et al., 2013). Soil properties, prevailing environmental conditions during application and management

practices govern the rate of ammonia volatilization from surface broadcast urea (Jones et al., 2013).

Currently, novel approaches aimed at controlling ammonia volatilization losses have centered on treating urea with urease inhibitors (stabilizers) or physically coating urea with a nutrient or polymer (controlled release fertilizers) coating to temporarily halt urea hydrolysis (Trenkel, 2010; Timilsena et al., 2015). Several studies have evaluated the viability of various urease inhibitors; N-(n-Butyl) triphosphoric triamide (NBPT), N-(n-propyl) triphosphoric triamide (NPPT), phenylphosphorodiamidate and hydroquinone, boron (B) and ammonium thiosulfate in minimizing ammonia volatilization. Among these urease inhibitors, NBPT was effective in reducing ammonia volatilization across wide range of soil and cropping systems (Rawluk et al., 2001; Engel et al., 2011; Griggs et al., 2007; Dillon et al., 2012; Tian et al., 2015). In flooded rice fields across the mid-southern United States, NBPT drastically reduced ammonia volatilization by 50 – 80% compared to urea (Norman et al., 2009; Roger et al., 2015). In both trials, the authors reported that NBPT treated urea resulted in increased rice grain yield compared to untreated urea. Addition of NBPT at the recommended rate of 0.8 g kg<sup>-1</sup> (Agrotain Ultra, KOCH) can be expensive and unattractive to commercial rice producers. Laboratory studies have also shown that urea coated with 5% boric acid reduced ammonia volatilization by 72% (Pursell et al., 2014). The results from laboratory study presented in the previous chapter confirmed the inhibitory effect of B on ammonia volatilization across multiple soil types. Boron compounds have been reported to control ammonia volatilization losses (Tabatabai, 1977; Singh et al., 2013). Ammonia volatilization and yield response studies focused on the effect of boron use alone or in conjunction with a micronutrient coated urea fertilizer is limiting.

Reduction in ammonia volatilization from polymer-coated urea fertilizers has been documented on rice fields (Tian et al., 2015). Nutrient-coated urea such as sulfur coated urea has been effective at minimizing ammonia volatilization in field studies for crops other than rice (Jantalia et al., 2012). However, the effects of polymer- and nutrient-coated urea fertilizers on ammonia volatilization are inconsistent across cropping systems and soil type (Xu et al., 2012; Tian et al., 2015). This suggests that the use of coated urea fertilizers may be an unreliable approach alone in minimizing ammonia volatilization. Furthermore, the inhibitory effect of coated urea fertilizers on ammonia volatilization and improved nitrogen use efficiency does not always result in higher grain yield. Several advances have been made to minimize ammonia volatilization by chemical and physical means independently; however, efforts are also being made to develop N fertilizers that simultaneously utilize multiple approaches to address ammonia volatilization as well as other nutritional deficiencies often encountered in crop production (Frame et al., 2012). This multipronged approach often includes the addition of micronutrients as a surface coating or a composite granule which improves the distribution of micronutrients that are only required by plants in minute quantities. Zinc deficiency is a common nutrient deficiency in flooded rice production. As such, zinc fertilization is often used in mid-South US rice production (Harrell et al., 2015). Studies have shown that 0.5 g kg<sup>-1</sup> NBPT have potential to reduce ammonia volatilization, although it may not be efficient as the recommended rate across different soil type (Rawluk et al., 2001). Combining a low concentration of NBPT with B with a nutrient coated urea may improve the reliability of a nutrient coated urea fertilizer to effectively minimize ammonia volatilization and increase rice productivity across different soils and cropping systems. Experimental zinc sulfate coated urea (ZSCU) fertilizers with or without urease inhibitors have been recently developed (Brooks Whitehurst Associates Inc., New

Bern, NC). The urease inhibitors contained in some of the experimental ZSCU fertilizers included NBPT and/or B. Preliminary research has demonstrated that NBPT treated urea used in combination with a nutrient coating can reduce ammonia volatilization (Frame et al., 2012).

Most of the field trials that have been conducted to evaluate ammonia volatilization in drill-seeded, delay-flood rice production in mid-southern U.S.A. have focused on NBPT and polymer-coated urea. However, none have quantified ammonia volatilization and grain yield potential of nutrient-coated urea in combination with NBPT and/or B fertilizer in delayed flood rice production systems. The objectives of this study were to: (1) quantify ammonia volatilization losses from surface applied experimental ZSCU fertilizers under field conditions, and (2) evaluate the effect of experimental ZSCU fertilizer use on biomass, grain yield, and nutrient use efficiency (NUE) in a delayed flood rice production system.

### **3.2 Materials and Methods**

#### **3.2.1 Study Site and Soil**

Field ammonia volatilization and yield trials were carried out for two years (2014 – 2015) on adjacent fields at the H. Rouse Caffey Rice Research Station, near Crowley, LA (N 30° 14.840' W 92° 21.196'). The fields for both years were managed in a rice-fallow rotation for over 30 years. The soil was a Crowley silt loam (Fine, smectitic, thermic Typic Albaqualfs) (Soil Survey Staff, NRCS, USDA, 2016). Composite soil samples for both years were collected from surface soil to a depth of 10 cm. The soils were air dried, sieved through a 2 mm sieve and analyzed for selected chemical and physical properties. Soil pH was analyzed in 1:1 soil to water ratio (Thomas, 1996). The particle size distribution of soil was determined using the hydrometer method (Gee and Or, 2002). Total soil N and C were determined by dry combustion analysis using a LECO TruSpec CN analyzer (LECO, Corp., St. Joseph, MI). Organic matter was

determined using the Wakley-Black method (Nelson and Sommers, 1999). Nutrients were determined using the Mehlich III soil test extraction (Mehlich, 1984). Elemental concentrations in the extract were measured using inductively coupled plasma atomic emission spectroscopy. Mean values of selected soil properties are presented in Table 3.1.

Table 3.1 Physio-chemical properties of study sites in 2014 and 2015.

Year	Texture <sup>†</sup>	pH	OM <sup>‡</sup> g kg <sup>-1</sup>	Mehlich III extractable nutrient levels						
				P	K	Ca	Mg mg kg <sup>-1</sup>	S	Na	Zn
2014	SL	7.40	14.4	6.7	55.2	1595	265	9.1	58.7	4.6
2015	SL	7.61	15.0	26.0	76.0	1641	231	6.7	111	9.0

<sup>†</sup>USDA textural classification; SL, Silt loam.

<sup>‡</sup>OM, Organic matter.

### 3.2.2 Volatilization Trials

Ammonia volatilization losses were monitored using the semi-open, static chamber method. This method has shown to be equally effective in evaluating the ammonia volatilization potential between N fertilizers as compared to other commonly used methods (McGinn and Janzen, 1997). The chambers were constructed using 14 cm (diameter) by 60 cm (height) transparent Plexiglas cylinders (Griggs et al., 2007; Dillon et al., 2012). The two (2014) or three (2015) tubes were installed within a plot in the middle drill-row. Each tube contained three rice seedlings. Pre-flood N was surface applied at a rate of 134 kg ha<sup>-1</sup> into each tube by hand at the 4- to 5-leaf stage of development. A 2.54 cm thick circular polyurethane foam sponge treated with 0.73 M H<sub>3</sub>PO<sub>4</sub> and 33% glycerol was tightly placed in each chamber 28 cm above the soil surface to capture ammonia volatilized from the fertilizer. A second treated sponge was placed above flush with the top of the chamber, 15.2 cm above the first sponge, to absorb atmospheric ammonia. A cross section of PVC pipes was fix on top of the chambers and then covered with 5 bucket to allow air circulation and protect the chambers from rain. The sponges were replaced 1,



3, 5, 7, 9, 11 and 15 d after N fertilization. Once removed, sponges were placed in Ziploc bags and transported to the lab for analysis. Ammonium was extracted from the sponges with 2 M KCl. The ammonium concentration from the extract was determined with an automated QuikChem<sup>®</sup> 8500 Series 2 flow injection analyzer using salicylate- hypochlorite method (QuikChem<sup>®</sup> Method 12-107-06-2-H) (Lachat Instrument, Loveland, CO).

Eight total N fertilizer sources were evaluated in the ammonia volatilization field trial in 2014. Five of the eight N fertilizer sources were experimental ZSCU fertilizers which were labeled as RCO1, RCO2, RCO3, RCO4, and RCO5 (Whitehurst Associates Inc., New Bern, NC). The nutritional concentrations of the ZSCU fertilizers are listed in detail in Table 3.2. Briefly, RCCO3 was prepared by coating urea with a finely ground zinc sulfate using a liquid binder. RCO2 was prepared in a similar fashion as RCO3 except 1.0 g B kg<sup>-1</sup> was added to the liquid binder. RCO5 was similar to RCO2 except the B concentration in the binder was increased to 1.7 g kg<sup>-1</sup>. RCO1 was the same as RCO3 except the urea was treated with NBPT at a rate of 0.3 g kg<sup>-1</sup> prior to binding the zinc sulfate. RCO4 was similar to RCO5 except the urea was treated with NBPT at a rate of 0.3 g kg<sup>-1</sup> prior to binding the zinc sulfate. Urea, urea treated with 0.9 g kg<sup>-1</sup> NBPT (Arborite Ag, Weyerhaeuser Company, Vanceboro, NC), and a 1:1 physical blend of urea treated with 0.9 g kg<sup>-1</sup> NBPT + zinc sulfate were also included in the volatilization experiment to serve as a comparison for the experimental ZSCU fertilizers. An unfertilized check was included to normalize the volatilization data and was not used in the statistical analysis.

In 2015, the NBPT percentage in the experimental ZSCU fertilizers was increased from 0.3 to 0.6 g kg<sup>-1</sup> and two additional experimental ZSCU fertilizers were evaluated in the field volatilization trials. The additional ZSCU fertilizers contained a calcium sulfate coating and were labeled as RCO1S (RCO1+CaSO<sub>4</sub> coating) and RCO4S (RCO4+CaSO<sub>4</sub> coating). Comparison

treatments in 2015 included urea and urea treated with 0.9 g kg<sup>-1</sup> NBPT. A total of nine fertilizer treatments were evaluated. An unfertilized treatment was also included in 2015 to normalize the volatilization data and was not included in the statistical analysis.

Table 3.2 Elemental composition and concentration of experimental zinc sulfate coated urea (ZSCU) fertilizer evaluated in study.

ZSCU <sup>†</sup>	N	P	Ca	S	B	Zn	NBPT <sup>‡</sup>
	-----g kg <sup>-1</sup> -----						
RCO3	389	54	0.0	12	0.0	20	0.3 (0.0)
RCO2	392	55	0.0	11	1.0	20	0.3 (0.0)
RCO5	392	55	0.0	11	1.7	20	0.3 (0.0)
RCO1	392	55	0.0	11	1.0	20	0.3 (0.6)
RCO4	392	55	0.0	11	1.7	20	0.3 (0.6)
RCO1S	392	55	3.0	11	1.0	20	0.3 (0.6)
RCO4S	392	55	3.0	11	1.7	20	0.3 (0.6)

<sup>†</sup>ZSCU, Zinc sulfate coated urea fertilizer.

<sup>‡</sup>NBPT, N-(n-butyl) thiophosphoric triamide. The concentration of NBPT was increased from 0.3 g kg<sup>-1</sup> in 2014 to 0.6 g kg<sup>-1</sup> in 2015.

### 3.2.3 Yield Trials

The yield trials were conducted at the same time as the volatilization trials on adjacent plots. All fertilizer treatments included in the volatilization trials were also included in the yield trials each year. However, the yield trials included two N rates, 67 and 134 kg ha<sup>-1</sup>. A control plot without N fertilization was included within each block. Two N fertilizer sources were added to the 2015 yield trial that were not included in the 2015 volatilization trial. These included a 1:1 physical blend of urea + zinc sulfate and a 1:1 physical blend of urea treated with 0.9 g kg<sup>-1</sup> NBPT + zinc sulfate. Unfertilized N plots were also included to evaluate nitrogen use efficiency (NUE) of the various N fertilizer sources.

The rice variety used in 2014 and 2015 was CL152 and CL111, respectively. The CL152 rice variety has superior lodging resistance, and good grain quality and milling (Oard et al.,

2013a). The CL111 rice variety is considered a high yielding, very early maturing long grain (Oard et al., 2013b). Rice was drill-seeded at 359 seed m<sup>2</sup> to a depth of 1.27 cm on 13 March, 2014 and 19 March, 2015 with Almaco heavy-duty grain drill (Almaco, Iowa) equipped with double-disk openers. Each plot was 1.24 m wide by 4.88 m long and consisted of seven rows spaced 20 cm apart. Phosphorus fertilizer was surface broadcast at planting at a rate of 67 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup> using triplesuper phosphate (0-46-0). Potassium was surface broadcast at planting as potash (0-0-60) at a rate of 67 kg K<sub>2</sub>O ha<sup>-1</sup>. Fertilizer N was surface broadcast as a single pre-flood application at the 4- to 5-leaf stage of rice development. Fields were flooded to a depth of approximately 10 cm 10 d after N fertilization. Standard agronomic and pest management practices were conducted during the growing season based on state recommendations (Harrell et al., 2015). Individual rice plots were harvested using a Wintersteiger Delta Combine (Wintersteiger, Inc., Salt Lake City, UT 84116-2876) equipped with a HM800 Harvest Master Grain Gauge system (Juniper Systems, Inc., Logan, UT, USA). Rough grain yield was adjusted to a moisture content of 120 g kg<sup>-1</sup>.

Aboveground plant samples were hand harvested on 6 August, 2014 and 28 July, 2015 from 0.9 m linear row of the middle drill-row at 50% heading in order to determine plant biomass, total N uptake and NUE. Biomass was determined by drying the plant samples at 60°C in a forced air drier until uniform weights were attained. The estimate of NUE was determined using the apparent nitrogen recovery efficiency method (Snyder and Bruulsema, 2007) and was calculated as: 
$$NUE = [(N \text{ removed from fertilized plot} - N \text{ removed from unfertilized plot}) / \text{total N applied}] * 100.$$

### 3.2.4 Statistical Analysis

A randomized complete block design with four replications was used in both the yield and volatilization trials. Data was analyzed using the PROC MIXED procedure in SAS 9.4 (SAS Institute, 2013). Nitrogen source and rate were considered fixed effects while block was considered a random effect. Orthogonal contrasts were used to compare significant treatment effects.

## 3.3 Results and Discussion

### 3.3.1 Ammonia Volatilization

Cumulative ammonia loss at each sampling period for the 15 d study in 2014 and 2015 is shown in Fig. 1. Total volatilization loss at the end of the 15 d trial for both years is presented in Table 3.3. In 2014, appreciable volatilization from urea and the experimental ZSCU fertilizers did not occur until 3 d after fertilization (Fig. 1). The low volatilization rate over the first 3 d after N fertilization was most likely due to soil moisture at the time of application which slowed urea hydrolysis. Previous research has shown that surface soil moisture at the time of fertilizer application can significantly influence urea hydrolysis (Rochette et al., 2009a; 2009b; Jones et al., 2013). The volatilization loss rate from urea and all experimental ZSCU fertilizers was much higher between 3 and 11 d after fertilization. Ammonia captured 11 d after for urea the ZSCU fertilizers 11 d after fertilization was minimal and tended to reach equilibrium. The low volatilization rate after 11 d post fertilization can be partially explained by the establishment of the flood. Once a soil is submerged and the soil becomes anaerobic, ammonia becomes stable and volatilization ceases. Ammonia volatilization from urea treated with NBPT and physically blended with zinc sulfate was less than 1% until 7 d after fertilization, increased to approximately 3.1% by 11 d after fertilization, and then became stable. Total cumulative

ammonia volatilization loss 15 d after fertilization differed significantly between some N fertilizer sources in 2014 (Table 3.3). Urea lost which volatilized 15 % of total N applied 15 d after application.

The total ammonia loss from urea treated with NBPT 15 d after application was only 3 %, representing an 80% reduction compared to urea. The inhibitory effect of NBPT on ammonia volatilization observed in present study is in agreement with previous studies (Dillion et al., 2012). Urea treated with NBPT volatilized less ammonia because the NBPT delays urea hydrolysis by occupying the microsites from which urea enzymes attacks urea (Amtul et al., 2002). The slow hydrolysis of urea prevented the rapid rise in soil pH which serves as a catalyst for conversion of ammonium to ammonia (Jones et al., 2013). Moreover, since urea hydrolysis is relatively slow,  $\text{NH}_4^+$  released is quickly retained on soil surface, consequently limiting its availability for conversion into ammonia (Francis et al., 2008). Urea treated with NBPT did not show appreciable N losses due to ammonia volatilization until 5 d after application. Total cumulative ammonia loss from urea over the 15 d trial was 22.5% which was significantly higher than any other fertilizer source (Table 3.3).

Total cumulative ammonia loss from experimental ZSCU fertilizers in increasing order was  $\text{RCO4} (10.6\%) < \text{RCO1} (11.3\%) < \text{RCO5} (12.0\%) < \text{RCO3} (13.1\%) < \text{RCO2} (13.3\%)$ .  $\text{RCO3}$  (physical coating only) decreased ammonia volatilization by 13% over urea. The loss from  $\text{RCO3}$  was statistically similar to urea which is consistent with previous finding Hawke and Baldock (2010), but in contrast to observation by Frame et al. (2012) where significant reduction in urea volatilization levels was reported. This confirm report from previous studies that ammonia loss from coated urea fertilizers are generally higher compared to NBPT treated urea (Tian et al., 2015). The  $\text{RCO2}$  and  $\text{RCO5}$  which comprised of 1.0 and 1.7 g B  $\text{kg}^{-1}$  in addition to

the zinc sulfate coating reduced ammonia volatilization by 11 and 20%, respectively, compared to urea but the increase was not significant. The lack of difference in the amount of ammonia loss from ZSCU fertilizers containing B as compared to urea contradicts findings in the controlled environment study. The lack of difference in ammonia loss may be attributed to abrasion of the zinc sulfate coating which may have caused fractures and increase the urea decomposition and consequently ammonia volatilization (Bierman et al., 2015). Furthermore, urea coated with boric acid can melt and decompose more quickly than urea alone at lower relative humidity (Pursell et al., 2013). During fertilizer application, some of the coatings appear to dissolve leaving the urea exposed with no protection. This may partly explain the lack of difference in ammonia loss between experimental fertilizer and urea. Among the experimental fertilizers evaluated, RCO4 and RCO1 (ZSCU fertilizers containing B and NBPT) were most effective in minimizing ammonia volatilization in comparison to urea. RCO1 and RCO4 significantly reduced ammonia loss by 25 and 29%, respectively compared to urea. The reduction in comparison to urea was similar to that reported for calcium sulfate and potassium sulfate coated urea containing NBPT (Frame et al., 2012). The varying B concentration in ZSCU fertilizer with NBPT did not influence the amount of ammonia volatilized. Urea treated with NBPT volatilized the same amount of ammonia as RCO1 and RCO4 (Table 3.3). This observation implies that treating urea granules with  $0.6 \text{ g kg}^{-1}$  NBPT and boron prior to coating with zinc sulfate is effective in reducing ammonia loss even under conditions that favor lower ammonia volatilization from urea.

Cumulative ammonia loss from urea in 2015 was 1.5 times greater than 2014 (Table 3.3). In 2015, ammonia volatilization from urea and all experimental ZSCU fertilizers began much earlier and was detectable 1 d after fertilization (Fig. 3.1). Volatilization losses from urea and the ZSCU fertilizers were rapid for the first 5 d after fertilization and then began to taper off. The

ammonia loss during this period accounted for nearly 17.2% of total N applied. The increased rate of volatilization during the first few days after application observed in 2015 was likely due to environmental conditions such as the higher temperature at fertilization in 2015 (Fig. 3.2) and a higher soil moisture as compared with 2014. Surface soil moisture and warmer temperature during fertilizer application may have played a role in the increase rate of urea hydrolysis and volatilization in 2015 (Rochette et al., 2009; Jones et al., 2013). The total ammonia loss reported in present study is consistent with previous studies in the mid-southern United State (Griggs et al., 2007; Dillion et al., 2012; Golden et al., Rogers et al., 2015). In 2015, cumulative ammonia volatilization loss 15 d after application differed significantly among N fertilizer sources (Table 3.3). The total amount of ammonia volatilized from each N fertilizer is shown in Table 3.3. The greatest cumulative ammonia loss occurred on plots fertilized with urea (22.5%).

The peak daily ammonia volatilization for urea treated with NBPT occurred between day 6 and 7 in comparison to urea which occurred within the first 3 d. Cumulative ammonia volatilization from urea treated with NBPT 15 d after application was 5.4% in 2015. Urea treated with NBPT drastically reduced urea volatilization levels by 76% during the 15 d trial. The inhibitory effect of NBPT on ammonia volatilization is similar to those reported in literature (Rawluk et al., 2001).

Cumulative ammonia volatilization loss from all experimental ZSCU fertilizers 15 d after fertilization is shown in Table 3.3. During this period, RCO2, RCO1, RCO5, RCO4, RCO4S, RCO3, and RCO1S volatilized 6.7, 9.5, 11.6, 14.2, 15.3, 16.9, and 17.2% of total N applied respectively. Application of RCO3 (ZSCU fertilizer with only physical coating) significantly reduced urea volatilization levels by 25% (Table 3.3). The lower loss does give credence that the physical coating on urea can delay urease attack, slow urea hydrolysis and minimize ammonia

volatilization when conditions favor ammonia volatilization (Frame et al., 2012). Addition of B to physical coating (RCO2 and RCO5) significantly reduced ammonia volatilization by 49 – 70% compared to urea fertilizer. Ammonia loss from RCO3 was significantly higher than RCO2 but similar to RCO5. Laboratory studies have shown that urea coated with boric acid or boron compound can significantly decrease ammonia volatilization by 30 – 70% (Pursell et al., 2014). Cumulative ammonia loss from experimental ZSCU fertilizers containing boron combined with 0.6 g kg<sup>-1</sup> NBPT (RCO1 & RCO4) significantly reduced ammonia loss by 37 – 58% in comparison to urea. The loss from RCO1 & RCO4 was similar to that from RCO2, RCO3 and RCO5. The results from present study suggest that additional coating of urea granules with 0.6 g kg<sup>-1</sup> NBPT prior to coating with boron and zinc sulfate did not provide additional benefit. The ammonia loss from RCO1S and RCO4S (15.3 and 17.2%) were not significantly different from urea despite a 24 – 32% reduction compared to urea. In comparison with the other ZSCU fertilizers, the ammonia loss from RCO1S and RCO4S were higher than RCO1 and RCO2 fertilizers. Also, the ammonia loss from RCO1S and RCO4S fertilizers was 3.2 and 2.9 times greater compared to NBPT treated urea.



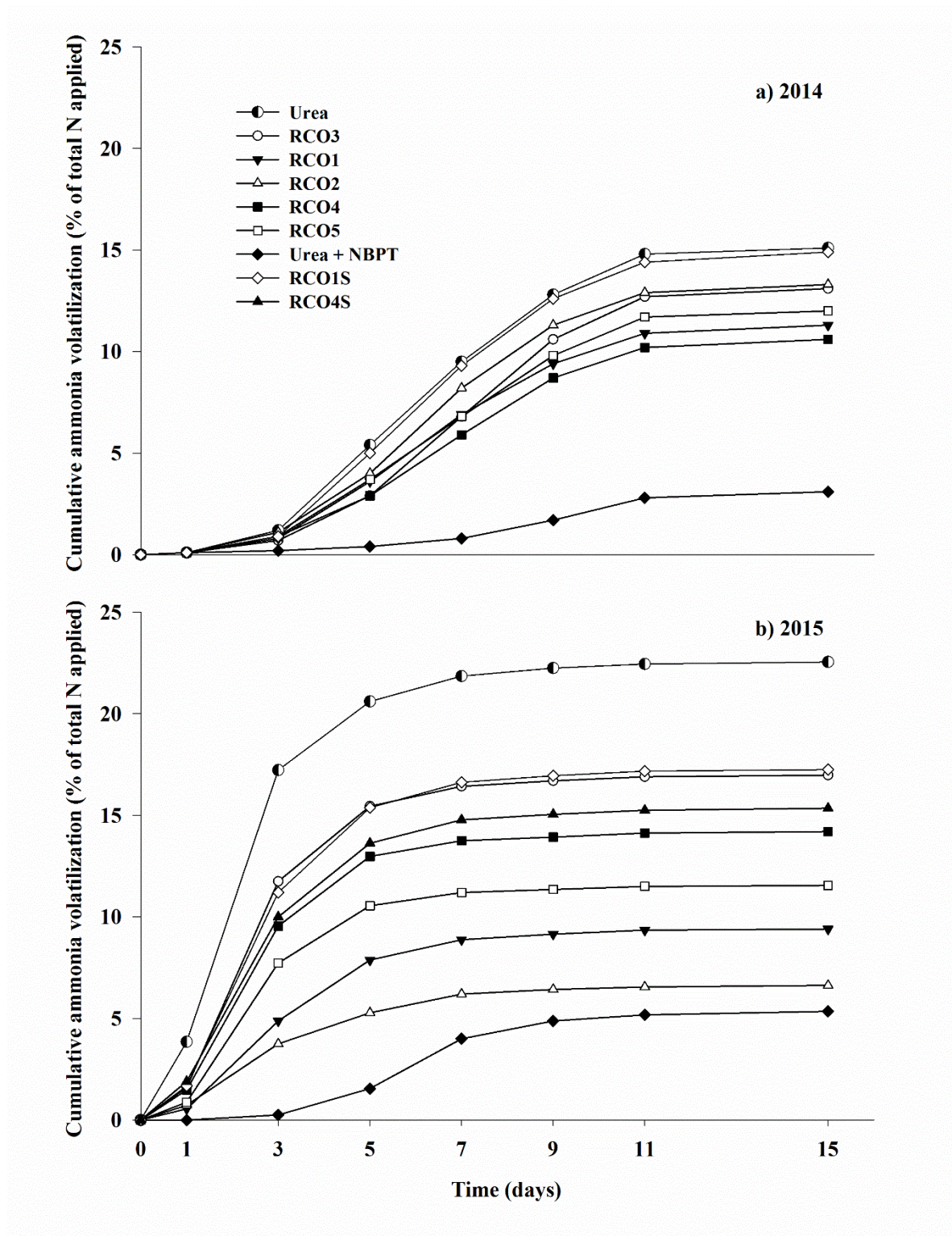


Figure 3.1 Mean cumulative N loss from urea, urea treated with NBPT, and experimental zinc sulfate coated urea (ZSCU) fertilizers for 15 d after application on Crowley silt loam in a) 2014 and b) 2015.

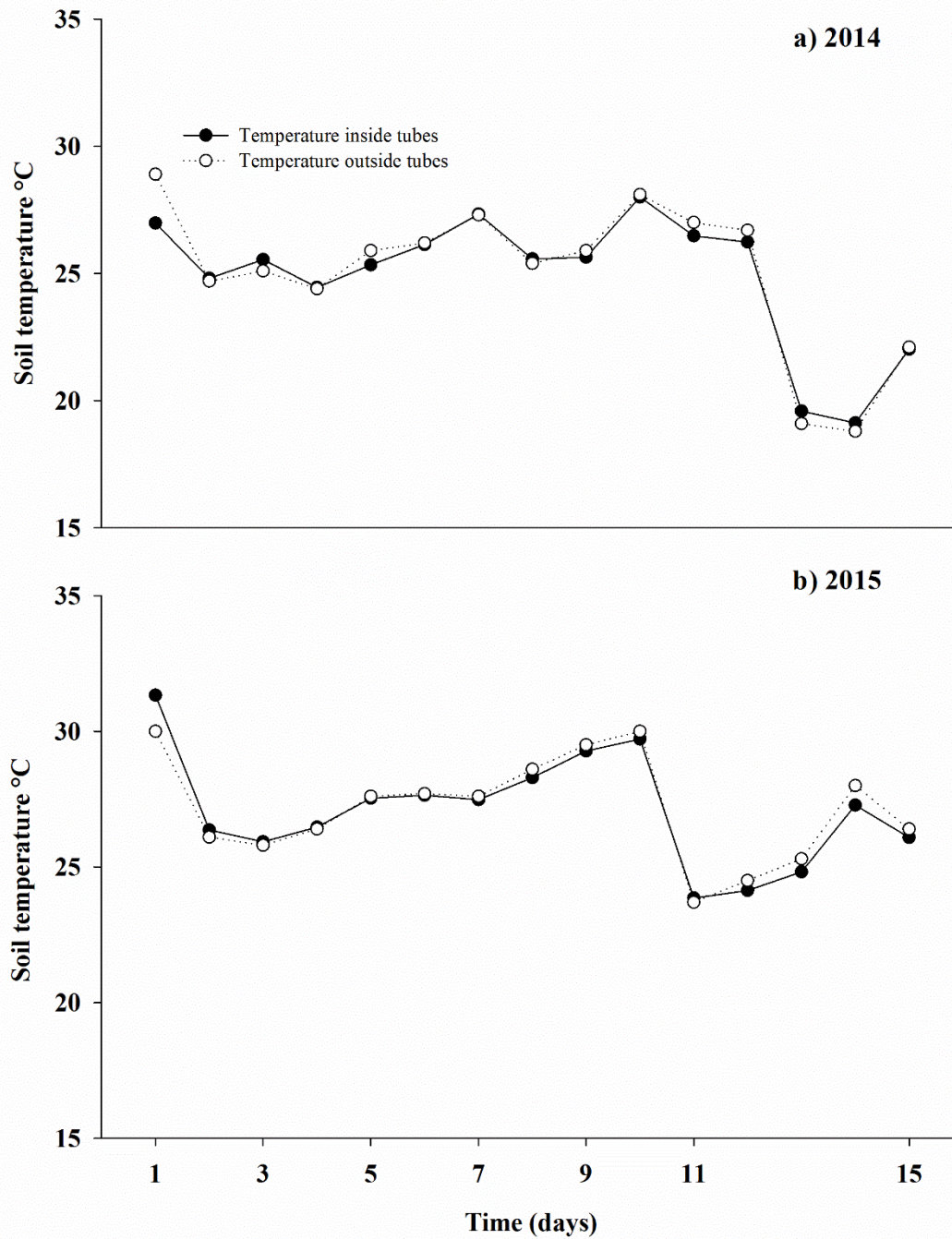


Figure 3.2 Mean daily temperatures inside and outside ammonia volatilization chambers in a) 2014 and b) 2015.



Table 3.3 Cumulative ammonia volatilization loss from N fertilizer sources 15 d after application in 2014 and 2015.

N fertilizer source	2014	2015
	-----%-----	
Urea	15.0 a	22.5 a
Urea + ZnSO <sub>4</sub>	14.9 a	-
Urea + NBPT	-	5.4 e
Urea + NBPT + ZnSO <sub>4</sub>	3.1 c	-
RCO3	13.1 ab	16.9 b
RCO2	13.3 ab	6.7 e
RCO5	12.0 ab	11.6 cd
RCO1	11.3 b	9.5 de
RCO4	10.6 b	14.2 bc
RCO1S	-	17.2 b
RCO4S	-	15.3 bc

<sup>†</sup>NBPT, N-(n-butyl)thiophosphoric triamide; ZnSO<sub>4</sub>, Zinc sulfate; ZSCU, Zinc sulfate coated urea fertilizer; RCO3, ZSCU only; RCO2, ZSCU+1.0 g B kg<sup>-1</sup>; RCO5, ZSCU+1.7 g B kg<sup>-1</sup>; RCO1, ZSCU+1.0 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO4, ZSCU+1.7 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO1S, RCO1+0.3 g Ca kg<sup>-1</sup>; RCO4S, RCO4+0.3 g Ca kg<sup>-1</sup>; Urea + ZnSO<sub>4</sub>, Zinc sulfate was added to urea to supply equivalent Zn from ZSCU fertilizer; Urea + NBPT, NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea; Urea + NBPT + ZnSO<sub>4</sub>, zinc sulfate was added to NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea. Means followed by the same letters within each column are not significantly different *P*(0.05).

### 3.3.2 Grain Yield

The average grain yield from control plots was (7538 kg ha<sup>-1</sup>) which was typically higher than reported in other studies (Griggs et al., 2007; Norman et al., 2009). Nonetheless, studies have also reported very high rice grain yield from unfertilized N plot in drill seeded delay-flooded rice production system (Tubana et al., 2012). The relatively high yield from unfertilized plots suggests that the soil supplied appreciable from N mineralization. A significant N source x rate interaction for grain yield was evident in 2014 (Table 3.4). However, the differences between N sources are reported and discussed for each application rate separately to present results in a manner that generate meaningful comparisons. The mean grain yield for N fertilizer

sources at the 67 kg N ha<sup>-1</sup> rate and 134 kg N ha<sup>-1</sup> rate in 2014 are shown in Table 3.7. Grain yield was significantly different among N sources at the 67 kg N ha<sup>-1</sup> rate but similar at the 134 kg N ha<sup>-1</sup> rate in 2014 (Table 3.5). Grain yield did not differ significantly between urea (10199 kg ha<sup>-1</sup>) and urea: zinc sulfate blend (10286 kg ha<sup>-1</sup>) at the 67 kg N ha<sup>-1</sup> suggesting that the addition of ZnSO<sub>4</sub> to urea during preflood N application did not impact grain yield. Interestingly, the rice grain yield from plots fertilized using urea treated with NBPT (9908 kg ha<sup>-1</sup>) were statistically similar to that of urea (with/without ZnSO<sub>4</sub>) at the 67 kg N ha<sup>-1</sup> (Table 3.7). Sufficient N supply from the soil is responsible for the lack of difference for rice grain yield. The grain yield for the experimental ZSCU fertilizers; RCO3, RCO2, RCO5, RCO1, RCO4 applied at 67 kg ha<sup>-1</sup> were 9129, 8772, 9609, 8503, and 10261 kg N ha<sup>-1</sup>, respectively. RCO3 (physically coating only) did not improve rice grain yield over urea and hence did not provide addition benefit. RCO2 (Physical coating plus 1.0 g B kg<sup>-1</sup>) was out yielded by urea but there was no significant difference between RCO5 (Physical coating plus 1.7 g B kg<sup>-1</sup>). Zinc sulfated coated urea fertilizers with 1.0 g B kg<sup>-1</sup> and 0.6 g kg<sup>-1</sup> NBPT were lower than urea fertilizers. This observation highlights some of the inconsistencies associated with coated fertilizers reported in other studies (Tian et al., 2015). The highest rice grain yield among experimental ZSCU fertilizers was observed in RCO4 (1.0 g B kg<sup>-1</sup> and 0.6 g kg<sup>-1</sup> NBPT) which was statistically similar to RCO3 and RCO5 but out yielded RCO1 and RCO2.

The lack of grain yield difference among N fertilizer treatments at 134 kg ha<sup>-1</sup> suggests that ammonia volatilization did not limit grain yield at this rate in 2014 (Table 3.3; Table 3.7). This may be partly explained by rainfall events following fertilizer application. There was 2 rainfall events (39 mm) 8 d after fertilizer application which coincided with periods close to maximum daily ammonia volatilization in 2014 (Fig. 3.1). The rainfall incorporated urea

granules and suppressed ammonia volatilization. As such, the ammonia losses reported in the chambers may be higher than in the open field. Holcomb et al. (2011) noted that application of 14.6 mm after urea application can decrease ammonia volatilization by 90%. Furthermore, the high grain yield from control plots ( $6413 \text{ kg ha}^{-1}$ ) indicate that the soil may have supplied sufficient N to counteract any N loss via ammonia and other processes; hence grain yield was limited by factors other than N.

Grain yield in 2015 was generally lower for all the treatment compared to 2014. Greater cumulative ammonia volatilization losses from N fertilizers in 2015 than 2014 (Fig. 3.2) may partly explain the difference in grain yield. Furthermore, the relatively high grain yield from control plot suggests that N from the soil may have compensated N losses via ammonia volatilization. Mean rice grain yield from N fertilizer treatment in 2015 is presented in Table 3.8. There was no significant interaction effect on rice grain yield in 2015; however N sources and rate resulted in different grain yields (Table 3.4). The average grain yield pooled across application rate from plots fertilized with urea was  $6725 \text{ kg N ha}^{-1}$  in 2015. Addition of zinc sulfate to urea ( $6920 \text{ kg N ha}^{-1}$ ) did not significantly increase grain yield as compared to urea only. The grain yield reported in present study is lower than reported from previous study on the same soil type (Dillion et al., 2012). Grain yield from urea treated with  $0.9 \text{ g kg}^{-1}$  NBBT was not significantly different compared to urea treated with  $0.9 \text{ g kg}^{-1}$  NBBT and zinc sulfate (Table 3.8). Urea treated with  $0.9 \text{ g kg}^{-1}$  NBPT significantly increased grain yield by 24 – 26% compared to urea in 2015. Studies that have compare urea to NBPT treated urea in drill seed delayed-flood rice production systems have reported significant grain yield increase (Norman et al., 2009) while other reported no significant increase (Dillion et al., 2012). The significant difference observed in 2015 and 2014 suggest that when conditions are ideal for greater

ammonia loss, addition of NBPT can result in significant grain yield increase over urea. The grain yield from experimental fertilizers was higher than urea and urea applied simultaneously with zinc sulfate with the exception of RCO3 (physical coating only). However, the yield increase from experimental fertilizers over urea were not significantly different (Table 3.8).

### 3.3.3 Aboveground Biomass

Biomass harvested in 2014 was not significantly influenced by the interaction between N rate and N fertilizer source (Table 3.4). The biomass from unfertilized N plot ( $6413 \text{ kg ha}^{-1}$ ) in 2014 was 18 – 35 % less compared to plots fertilized with N (Table 3.5). Biomass from unfertilized N plot in present study was exceptionally high and a deviation from those reported from previous studies from same fields (Linscombe et al., 2009; Linscombe et al., 2010). The aboveground biomass sampled at 50% heading from plots treated with N fertilizers in 2014 is presented in Table 3.5. Biomass differed significantly between N fertilizer rates; but was not significantly affected by N fertilizer sources in 2014 (Tables 3.4 and 3.5). The average biomass for RCO1, RCO5, RCO3, RCO2, Urea, Urea +  $\text{ZnSO}_4$  + NBPT, Urea +  $\text{ZnSO}_4$ , and RCO4 in 2014 was 7871, 8378, 8567, 8706, 8714, 8932, 9451, and 9925  $\text{kg ha}^{-1}$ , respectively. Shivay et al. (2008) did not also notice significant differences in rice straw yield between zinc sulfate coated urea fertilizers and urea fertilizers. Other studies have shown contrasting results of the effect of coated urea fertilizer application on biomass production in rice. For instance, coated urea fertilizers resulted in significant reduction biomass production in aerobic rice compared to urea (Rose, 2015). The author attributed the lower biomass yield to delayed early growth. The tissue N of rice plants in this study ( $10.1 - 12.7 \text{ g kg}^{-1}$ ) from fertilized plots coupled with the relatively high biomass yield from control plots suggest that the N was not a limiting factor to biomass. This may partly explain why the low ammonia volatilization losses from urea treated

with NBPT did not result in higher biomass compared to urea and the experimental ZSCU fertilizers (Table 3.3; Table 3.5). Mean biomass from the 134 kg N ha<sup>-1</sup> rate (9476 kg ha<sup>-1</sup>) was significantly higher than the 67 kg N ha<sup>-1</sup> rate (8115 kg ha<sup>-1</sup>).

The biomass yield for N fertilizer sources in 2015 is presented in Table 3.8. Biomass from control plots (3694 kg ha<sup>-1</sup>) was 40 – 51 % less than literature fertilized N plots (Table 3.8). The biomass yield of unfertilized plots is in agreement with results reported Rehman et al. (2012) wherein there was similar yield difference in biomass yield of rice plant with and without N fertilization. Inherently low N in unfertilized plots decreased the ability of plants from these plots to synthesize proteins, enzymes and metabolic processes essential for synthesis of energy, which ultimately limited plant biomass (Marschner, 2012). There was no significant interaction between N fertilizer source and N rate in 2015. Biomass was similar among N fertilizer sources but different for N rates (Table 3.4). Urea treated with NBPT (7124 kg ha<sup>-1</sup>) and urea treated with NBPT plus zinc sulfate (7481 kg ha<sup>-1</sup>) increased biomass in comparison to the other N fertilizers with the exception of RCO1S (6133 – 6677 kg ha<sup>-1</sup>). Nonetheless, these increases were statistically the same. The lack of differences suggests that N, which influences biomass was not limiting despite the significant differences in ammonia volatilization from N fertilizer sources (Marschner, 2012). The average biomass pooled across application rate for RCO3, RCO5, RCO4, RCO2, RCO4S, RCO1, and RCO1S were 6440, 6592, 6628, 6821, 7048, 7049, 7182, and respectively. Biomass yields from four of the experimental ZSCU fertilizers were higher than those from urea although the difference was not significant. As expected biomass increased with N fertilizer rate whereby biomass at the 134 kg N ha<sup>-1</sup> rate (7540 kg ha<sup>-1</sup>) was significantly higher compared to 67 kg N ha<sup>-1</sup> rate (6034 kg ha<sup>-1</sup>).

### 3.3.4 Nitrogen Uptake

Nitrogen uptake in 2014 differed significantly among N fertilizer sources and rates; but was not affected by their interaction (Table 3.4). Interestingly, the highest N uptake was numerically greatest for plots fertilized with urea applied simultaneous with zinc sulfate (111 kg ha<sup>-1</sup>). Although this N uptake was slightly higher than urea only (95.1 kg ha<sup>-1</sup>), the difference was not significant. Urea treated with NBPT (101 kg ha<sup>-1</sup>) did not significantly improve N uptake over urea. Mean N uptake pooled across application rate for RCO1, RCO5, RCO2, RCO3, and RCO5 were 86, 89, 90, 93, 95, and 104 kg N ha<sup>-1</sup>, respectively. There was no significant difference in N uptake among experimental fertilizers (Table 3.5). Lack of difference was not surprising considering N uptake strongly correlates with biomass yield. Nitrogen uptake pooled across N sources increased significantly with application rate. The N uptake at the 0, 67, and 134 kg N ha<sup>-1</sup> rates were 57, 82, and 110 kg ha<sup>-1</sup>, respectively. The N uptake from the highest rate was significantly higher compared to the lowest rate and unfertilized N plot.

Nitrogen uptake by rice in 2015 was significantly influenced by N fertilizer source x N rate interaction (Table 3.4); however, the differences between N sources are reported and discussed for each application rate separately in order to present results that generate meaningful comparisons. The N uptake for all the N sources at each application rate is reported in Table 3.10. Nitrogen uptake from plots fertilized with urea at the 67 kg N ha<sup>-1</sup> rate was 54.2 kg N ha<sup>-1</sup> which was comparable to urea applied simultaneous with zinc sulfate (Table 3.10). Urea treated with NBPT significantly increased N uptake by 17 – 33% compared to urea at 67 kg N ha<sup>-1</sup> rate. There was no difference in N uptake between NBPT-treated urea (63.7 kg N ha<sup>-1</sup>) and NBPT-treated urea applied simultaneous with zinc sulfate (72.2 kg N ha<sup>-1</sup>) (Table 10). The N uptake from RCO1, RCO4S, RCO5, RCO3, RCO2, RCO1S, and RCO4 applied at 67 kg N ha<sup>-1</sup> rate



were 47.3, 47.8, 51.5, 52.4, 53.5, 53.7, and 57.3%, respectively. Nitrogen uptake did not significantly differ among ZSCU fertilizer (Table 3.10). Among the five ZSCU fertilizers evaluated, only N uptake from RCO4 was statistically similar to NBPT-treated urea at 67 kg N ha<sup>-1</sup> rate. The N uptake from experimental ZSCU fertilizers was not significantly different in comparison to urea.

When urea was applied at 134 kg N ha<sup>-1</sup>, the rice took up 73.6 kg N ha<sup>-1</sup> which was statistically similar to urea applied simultaneously with zinc sulfate at the same rate (Table 3.10). Urea treated with NBPT improved N uptake by 29 – 38% in comparison to urea. Simultaneous application of NBPT-treated urea and zinc sulfate did not improve N uptake over NBPT-treated urea (Table 3.10). Physically coating urea with zinc sulfate (RCO3) did not affect N uptake compared to urea. The addition of boron (B) to the physical coating (RCO2 and RCO5) improved N uptake by 18% over urea; however this increase was not significant (Table 3.10). Application rate of B in ZSCU fertilizer did not affect N uptake. Nitrogen uptake from RCO5 and RCO3 were not significantly different from RCO3 fertilizers. Addition of NBPT to ZSCU fertilizers containing 1.0 g B kg<sup>-1</sup> (RCO2) increased N uptake over urea while that containing 1.7 g B kg<sup>-1</sup> (RCO5) did not affect N uptake compared to urea (Table 3.10). Nonetheless, N uptake from RCO1 and RCO4 were not significantly different from urea. The addition of calcium sulfate coating to RCO1 and RCO4 increase N uptake by 19 – 35%, respectively. However, only the N uptake from RCO4S applied at 134 kg N ha<sup>-1</sup> was significantly higher than urea (Table 3.10). The N uptake RCO4S was statistically similar to the other experimental ZSCU fertilizers with the exception of RCO3 and RCO4.

### 3.3.5 Nitrogen Use Efficiency

Nitrogen use efficiency in 2014 was not affected by the interaction of N source and rate as well as N source and rate effects in 2014 (Table 3.4). The NUE reported in 2014 was generally lower than documented in other studies. The lower NUE was expected considering that biomass and N uptake from the unfertilized N plots showed that the soil supplied substantial amount of N. Hence, there was sufficient N available to rice plant thereby decreasing the efficiency of applied N fertilizers. The above reason may partly explain the lack of significant difference among N fertilizer sources and rates in 2014.

Nitrogen use efficiency differed significantly among N source but was not affected by N rate in 2015 (Table 3.4). Nitrogen use efficiency from urea (35.3 %) was similar to that from simultaneous application of urea and zinc sulfate (31.0 %). Urea treated with NBPT (52.9 – 56.6%) significantly improved NUE compared to urea (Table 3.8). Physically coating urea with zinc sulfate (RCO3) did not significantly increase NUE over urea fertilizer and was significantly lower than NBPT-treated urea fertilizers. Zinc sulfate coated urea fertilizers containing B (RCO2 and RCO5) showed higher NUE compared to urea but the differences were not significant. RCO2 was statistically comparable to NBPT-treated urea while RCO5 was significantly lower than NBPT-treated urea. The NUE from plots fertilized with ZSCU fertilizers in combination with B and NBPT (RCO1 and RCO4) was similar to that of urea fertilized plots, RCO3, RCO2 and RCO5 (Table 3.8). However, the N use was less efficient compared to NBPT-treated urea. Although the extra CaSO<sub>4</sub> coating in addition to ZSCU containing NBPT and B did not significantly improved NUE over urea, its NUE was statistically similar to urea treated with NBPT.

Table 3.4 Test of fixed effect and interactions for biomass yield, N uptake, nitrogen use efficiency (NUE), and grain yield for 2014 and 2015.

Year	Source of variation	Biomass	N Uptake	NUE	Yield
2014	Rate	<.0001	<.0001	0.4341	<.0001
	N source	0.0729	0.0330	0.3002	0.0170
	Rate x N source	0.3910	0.1808	0.4894	0.0317
2015					
	N Rate	<.0001	<.0001	0.8359	<.0001
	N Source	0.4649	0.0009	0.0033	<.0001
	Rate x N source	0.0918	0.0191	0.1538	0.2424

Table 3.5 The effect of N fertilizer sources on biomass yield, N uptake, and nitrogen use efficiency (NUE) of rice at 50% heading in 2014

N source <sup>†</sup>	Biomass	N Uptake	NUE
	-----kg ha <sup>-1</sup> -----		%
Urea	8714 a	95.1 ab	50.9 a
Urea + ZnSO <sub>4</sub>	9925 a	111.1 a	52.3 a
Urea + NBPT + ZnSO <sub>4</sub>	8932 a	100.7 ab	47.1 a
RCO3	8567 a	92.7 ab	38.5 a
RCO2	8706 a	89.9 ab	45.2 a
RCO5	8378 a	89.1 ab	41.3 a
RCO1	7871 a	85.6 b	34.0 a
RCO4	9451 a	104.2 ab	48.4 a

Mean biomass and N uptake for control plots were 6413 and 56.6 kg ha<sup>-1</sup>, respectively.

<sup>†</sup>NBPT, N-(n-butyl)thiophosphoric triamide; ZnSO<sub>4</sub>, Zinc sulfate; ZSCU, Zinc sulfate coated urea fertilizer; RCO3, ZSCU only; RCO2, ZSCU+1.0 g B kg<sup>-1</sup>; RCO5, ZSCU+1.7 g B kg<sup>-1</sup>; RCO1, ZSCU+1.0 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO4, ZSCU+1.7 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; Urea + ZnSO<sub>4</sub>, zinc sulfate was added to urea to supply equivalent Zn from ZSCU fertilizer; Urea + NBPT + ZnSO<sub>4</sub>, zinc sulfate was added to NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea.

Means followed by the same letters within each column are not significantly different *P* (0.05).

Table 3.6 The effect of N rate effect on biomass yield, N uptake, and nitrogen use efficiency (NUE) of rice at 50% heading in 2014.

N rate	Biomass	N Uptake	NUE
	-----kg ha <sup>-1</sup> -----		%
67	8115 b	82.2 b	45.6 a
134	9479 a	110.2 a	42.4 a

Means followed by the same letters within each column are not significantly different *P* (0.05).

Table 3.7 Mean grain yield for N fertilizer sources at the 67 kg N ha<sup>-1</sup> rate and 134 kg N ha<sup>-1</sup> rate in 2014.

N source <sup>†</sup>	67	134
	-----kg ha <sup>-1</sup> -----	
Urea	10199 a	11152 a
Urea + ZnSO <sub>4</sub>	10286 a	10295 a
Urea + NBPT + ZnSO <sub>4</sub>	9908 a	10581 a
RCO3	9129 ab	10750 a
RCO2	8772 b	10921 a
RCO5	9609 ab	10524 a
RCO1	8503 b	10556 a
RCO4	10261 a	10986 a

Grain yield for control plots was 7538 kg ha<sup>-1</sup>

<sup>†</sup>NBPT, N-(n-butyl)thiophosphoric triamide; ZnSO<sub>4</sub>, Zinc sulfate; ZSCU, Zinc sulfate coated urea fertilizer; RCO3, ZSCU only; RCO2, ZSCU+1.0 g B kg<sup>-1</sup>; RCO5, ZSCU+1.7 g B kg<sup>-1</sup>; RCO1, ZSCU+1.0 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO4, ZSCU+1.7 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; Urea + ZnSO<sub>4</sub>, zinc sulfate was added to urea to supply equivalent Zn from ZSCU fertilizer; Urea + NBPT + ZnSO<sub>4</sub>, zinc sulfate was added to NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea.

Means followed by the same letters within each column are not significantly different *P* (0.05).

Table 3.8 The effect of N fertilizer sources on biomass yield, nitrogen use efficiency (NUE), and grain yield in 2015.

N source <sup>†</sup>	Biomass kg ha <sup>-1</sup>	NUE %	Yield kg ha <sup>-1</sup>
Urea	6677 a	35.3 cd	6725 b
Urea + ZnSO <sub>4</sub>	6133 a	31.0 d	6920 b
Urea + NBPT	7124 a	52.9 ab	9145 a
Urea + NBPT + ZnSO <sub>4</sub>	7481 a	56.6 a	9144 a
RCO3	6440 a	36.1 cd	6701 b
RCO2	6821 a	45.3 abc	7301 b
RCO5	6592 a	42.2 bcd	7408 b
RCO1	7049 a	36.7 cd	7363 b
RCO4	6628 a	39.2 cd	7026 b
RCO1S	7182 a	44.9 abc	7327 b
RCO4S	7048 a	43.2 abcd	7389 b

Mean biomass and grain yield for control plots were 3694 and 4045 kg ha<sup>-1</sup>, respectively.

<sup>†</sup>NBPT, N-(n-butyl)thiophosphoric triamide; ZnSO<sub>4</sub>, Zinc sulfate; ZSCU, Zinc sulfate coated urea fertilizer; RCO3, ZSCU only; RCO2, ZSCU+1.0 g B kg<sup>-1</sup>; RCO5, ZSCU+1.7 g B kg<sup>-1</sup>; RCO1, ZSCU+1.0 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO4, ZSCU+1.7 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO1S, RCO1+0.3 g Ca kg<sup>-1</sup>; RCO4S, RCO4+0.3 g Ca kg<sup>-1</sup>; Urea + ZnSO<sub>4</sub>, Zinc sulfate was added to urea to supply equivalent Zn from ZSCU fertilizer; Urea + NBPT, NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea; Urea + NBPT + ZnSO<sub>4</sub>, zinc sulfate was added to NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea.

Means followed by the same letters within each column are not significantly different *P* (0.05).

Table 3.9 The effect of N rate on biomass yield, nitrogen use efficiency (NUE), and grain yield in 2015.

N rate	Biomass kg ha <sup>-1</sup>	NUE %	Yield kg ha <sup>-1</sup>
67	6034 b	40.9 a	6357 a
134	7540 a	40.4 a	8303 b

Means followed by the same letters within each column are not significantly different *P* (0.05).

Table 3.10 Mean N uptake for N fertilizer sources at the 67 kg N ha<sup>-1</sup> rate and 134 kg N ha<sup>-1</sup> rate in 2015.

N fertilizer source <sup>†</sup>	67	134
	-----kg ha <sup>-1</sup> -----	
Urea	54.2 b	73.6 bcd
Urea + ZnSO <sub>4</sub>	53.5 b	58.5 d
Urea + NBPT	63.7 a	101.3 a
Urea + NBPT + ZnSO <sub>4</sub>	72.2 a	94.8 ab
RCO3	52.4 b	72.3 cd
RCO2	53.5 b	86.5 abc
RCO5	51.5 b	86.5 abc
RCO1	47.3 b	90.9 abc
RCO4	57.3 ab	69.5 cd
RCO1S	53.7 b	87.6 abc
RCO4S	47.8 b	99.3 a

<sup>†</sup>NBPT, N-(n-butyl)thiophosphoric triamide; ZnSO<sub>4</sub>, Zinc sulfate; ZSCU, Zinc sulfate coated urea fertilizer; RCO3, ZSCU only; RCO2, ZSCU+1.0 g B kg<sup>-1</sup>; RCO5, ZSCU+1.7 g B kg<sup>-1</sup>; RCO1, ZSCU+1.0 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO4, ZSCU+1.7 g B kg<sup>-1</sup>+0.3 g kg<sup>-1</sup> NBPT; RCO1S, RCO1+0.3 g Ca kg<sup>-1</sup>; RCO4S, RCO4+0.3 g Ca kg<sup>-1</sup>; Urea + ZnSO<sub>4</sub>, Zinc sulfate was added to urea to supply equivalent Zn from ZSCU fertilizer; Urea + NBPT, NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea; Urea + NBPT + ZnSO<sub>4</sub>, zinc sulfate was added to NBPT (Arborite Ag applied onto urea at 0.9 g kg<sup>-1</sup> NBPT)-treated urea.

Means followed by the same letters within each column are not significantly different *P* (0.05).

### 3.4 Conclusions

The goal of this study was to evaluate experimental zinc sulfate coated urea (ZSCU) fertilizers with different compositions as a reliable alternative to controlling ammonia volatilization and improving rice productivity. The cumulative ammonia volatilization from urea was 15.0 and 22.5% in 2014 and 2015, respectively. Urea treated with NBPT delayed ammonia volatilization and significantly reduced urea volatilization losses regardless of the amount of total ammonia loss. In contrast, the experimental ZSCU fertilizers were only effective in controlling ammonia volatilization when ammonia volatility was higher. The physical coating with zinc sulfate alone did significantly reduce ammonia volatilization in comparison to urea. Addition of

B to the physical coating had an additive effect in reducing ammonia volatilization whereas when ZSCU in combination with NBPT and B did not provide additive effect over physical coating. Overall, ammonia volatilization control was generally greater for urea treated with NBPT than the experimental ZSCU fertilizers evaluated in this trial. In the first year of study, the differences in ammonia volatilization did not influence biomass and nitrogen use efficiency. Rice plants receiving NBPT treated urea and experimental ZSCU fertilizers had similar biomass yield and NUE as urea. Grain yield was similar among all fertilizer treatments at 135 kg N ha<sup>-1</sup>. In the second year, biomass was similar for all N fertilizer sources but urea treated with NBPT out yielded all other N fertilizers. The results suggest that the experimental ZSCU fertilizers have potential to control ammonia volatilization but do not result in increased grain yield.

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## **Chapter 4. Evaluation of Zinc Sulfate Coated Urea Fertilizer as a Potential Zinc Source in Drill-seeded Delayed Flood Rice Production**

### **4.1 Introduction**

Zinc (Zn) deficiency is the most documented micronutrient deficiency in flooded rice fields in the mid-southern United States of America (Slaton et al., 2005; Harrell and Saichuk, 2016). Zinc is an essential micronutrient plays an integral role in several plant physiological functions such as structural integrity, protein synthesis and gene expression (Cakmak, 2000; Broadley et al., 2007; Palmer and Guerinot, 2009; Marschner, 2012). Zinc deficiency results in various symptoms which typically occur between the 2-leaf and mid-tillering stages in rice (Wissuwa et al., 2006). Visual Zn deficient symptoms commonly observed in seedling rice include basal chlorosis, bronzing of leaves, stunt growth and reduced tillering (Marschner, 2012; Sharma et al., 2013). In most cases, seedling rice that recovers from these symptoms will show delayed maturity and subsequently reduction in grain yield particularly for susceptible cultivar (Hafeez et al., 2012). In severe cases, the entire rice stand may be lost. Zinc deficiency in flooded rice fields has been attributed to a wide range of soil conditions: inherently low plant available Zn, high soil pH ( $> 7.0$ ), low redox potential, high soil organic matter and bicarbonate content, high plant available P and cold temperature (Alloway, 2008; Hafeez et al., 2012). Zinc deficiency in rice fields has increase with the cultivation of high yielding rice varieties, crop intensification, adoption of laser leveling techniques and improved purity of inorganic fertilizers (Slaton et al., 2001; Brye, 2006; Naik and Das, 2007; Graham et al., 2007).

Despite breeding efforts, Zn deficiency has intensified over the years. In order to identify and improve rice cultivar tolerant to Zn deficiency, soil and foliar fertilization are the most feasible means of addressing Zn deficiency (White and Broadley, 2005). Rice fields with low

plant available Zn are commonly ameliorated with zinc sulfate because of its high water solubility which can be easily blended with preplant P and K (Mikkelsen and Kuo, 1977; Stalon et al., 2005). According to Bashir (1999), ZnSO<sub>4</sub> fertilizer is very soluble and highly bioavailable when applied initially, however, bioavailability declines shortly because of transformation into insoluble Zn forms. Other sources such Zn chelates (Zn-EDTA, Zn-NTA) and products from natural organic ligands (Zn lignosulfonate) are used in rice fields across the United States (Slaton et al., 2005). Generally, organic Zn fertilizer sources are more effective in correcting Zn deficiency in comparison to inorganic source such as zinc sulfate; however, the high costs of organic Zn fertilizer limit use and application. Studies have investigated the effect of split application and Zn source as an alternative strategy to improve Zn availability in flooded rice production (Naik and Das, 2007). Naik and Das, 2007 reported that the effect of split application Zn fertilizer depended on zinc source. According to the authors, split application of zinc sulfate can improve rice yield while Zn EDTA did not affect grain yield as compared to respective single application.

In recent years, controlled release fertilizers, particularly nutrient-coated have gained increased attention. Nutrient-coated urea fertilizers are developed primarily to control ammonia volatilization losses and synchronize N release to meet plant demand; however, they can potentially mitigate other nutritional deficiencies (Trenkel, 2010; Timilsena et al., 2015). An added advantage for these innovative fertilizers is potential for a relatively even distribution of Zn considering large rates of application. The challenge in using controlled-release urea fertilizer is the amount of Zn that can be supplied as starter fertilizer because of its high N content. Generally, only 16.8 – 22 kg N ha<sup>-1</sup> starter N is recommended due to poor N management (Harrell and Saichuk, 2016). In order to evaluate controlled release urea fertilizer as a Zn source,

it must be managed as split application. An experimental zinc sulfate coated urea (ZSCU) was developed by Brooks Whitehurst Associates Inc. primarily to improve nitrogen use efficiency. The experimental ZSCU fertilizer may slowly release Zn to rice plant throughout the growing season as compared with  $\text{ZnSO}_4$  in which Zn is readily converted into less soluble forms that are not plant available. The physical coating and larger granule size of coated urea fertilizers can influence fertilizer distribution, and perhaps reduce recommendation rates. Previous studies that have evaluated ZSCU as a potential zinc source reported promising results in Zn uptake and grain yield (Shivay et al., 2015). However, these reported studies were conducted in rice production systems and soils that are quite different from mid-southern United States. Zinc fertilization is applied at preplant in rice field since Zn deficiency occurs between the 2-leaf and mid-tillering stages in rice. The experimental ZSCU fertilizers contain  $389.5 \text{ g N kg}^{-1}$  and only  $16.8 - 22 \text{ kg N ha}^{-1}$  preplant N is generally recommended (Harrell and Saichuk, 2016). When experimental ZSCU fertilizer is applied at  $16.8 - 22 \text{ kg N ha}^{-1}$  would only supply  $0.8 - 1.12 \text{ kg Zn ha}^{-1}$  which may be insufficient to correct Zn deficiency. As such, evaluating ZSCU fertilizers as Zn source requires a split application as a starter and pre-flood application. There are limited studies on the combination of starter and pre-flood Zn fertilization using ZSCU. The objective of this study was to evaluate the effect ZSCU and ZSCU: Zinc sulfate blend on plant biomass, grain yield, Zn uptake, and tissue elemental concentration in drill seeded delay-flood rice production system.

## **4.2 Materials and Methods**

### **4.2.1 Study Site and Soil**

A two year field trial was established at different sites on a Mowata Silt loam (Fine smectitic, thermic, Typic Glossaqualfs). The field were cultivated in soybean [*Glycine max* (L.)

Merr.] prior to the trial conducted in 2014 and 2015. Composite soil samples for both years were collected prior to the selection of each study sites to ensure that Zn was limiting. Also, composite soil samples were collected prior to the start of trial representing unfertilized Zn plots before starter fertilizer was applied to a depth of 10 cm. The soils samples were air dried, sieved through a 2 mm sieve and analyzed for selected chemical and physical properties. Soil pH was analyzed in 1:1 soil to water ratio (Thomas, 1996). The particle size distribution of soil was determined using the hydrometer method (Gee and Or, 2002). Total soil N and C were determined by dry combustion analysis using a LECO TruSpec CN analyzer (LECO, Corp., St. Joseph, MI). Organic matter was determined using the Wakley-Black method (Nelson and Sommers, 1999). Nutrients were determined using the Mehlich III soil test extraction (Mehlich, 1984). Elemental concentrations in the extract were measured using inductively coupled plasma atomic emission spectroscopy. Mean values of selected soil properties from unfertilized plots before starter fertilizer application are presented in Table 4.1.

Table 4.1. Physio-chemical properties of soil from study sites in 2014 and 2015.

Year	Texture <sup>†</sup>	pH	OM <sup>‡</sup>	Mehlich III extractable nutrient levels						
				P	K	Ca	Mg	S	Na	Zn
			g kg <sup>-1</sup>				mg kg <sup>-1</sup>			
2014	SL	5.3	11.0	10.5	34	557	122	1.4	70	2.4
2015	SL	6.5	8.3	6.7	39	1087	252	17.2	110	1.7

<sup>†</sup>USDA textural classification; SL, Silt loam.

<sup>‡</sup>OM, Organic matter.

#### 4.2.2 Zn Fertilizer Treatments

The zinc sources used in the trial were zinc sulfate and experimental zinc sulfate coated urea (ZSCU) fertilizer manufactured by Brooks Whitehurst Associates Inc. The experimental ZSCU fertilizer was manufactured by physically coating urea granules with zinc sulfate. The ZSCU fertilizer was characterized by Brooks Whitehurst Associates Inc. as containing 389.5 g N

kg<sup>-1</sup>, 54 g P<sub>2</sub>O kg<sup>-1</sup> 12 g S kg<sup>-1</sup> and 20 g Zn kg<sup>-1</sup>. The recommended soil application rate for both years (based on soil test results prior to the trial) was 11.2 kg Zn ha<sup>-1</sup>. Based on the soil test recommendation, five Zn starter rate were evaluated and this include: 0, 1.12, 2.8, 5.6, and 11.12 kg Zn ha<sup>-1</sup>. During N fertilization at the 4- to 5- leaf stage of rice development, four preflood Zn fertilizer treatments were administer to 1.12, 2.8, and 5.6 kg Zn ha<sup>-1</sup> starter rates. The preflood treatments include: 0, 2:1 Urea: ZSCU blend, 1:1 Urea: ZSCU blend, and ZSCU only. The total amount of Zn applied at each starter rate and preflood treatment is presented in Table 4.2.

Table 4.2 Total amount of Zn applied at each fertilizer treatment.

Starter rate	Preflood treatment	Total Zn applied
		kg Zn ha <sup>-1</sup>
0	0	0.0
1.12	0	1.1
	2:1 Urea: ZSCU	3.2
	1:1 Urea: ZSCU	4.3
	ZSCU	8.0
2.8	0	2.8
	2:1 Urea: ZSCU	4.9
	1:1 Urea: ZSCU	6.0
	ZSCU	9.7
5.6	0	5.6
	2:1 Urea: ZSCU	7.7
	1:1 Urea: ZSCU	8.8
	ZSCU	12.5
11.2	0	11.2

#### 4.2.3 Yield Trial

The field trial was conducted in plots measuring 1.27-m wide x 4.88-m long. The rice variety used in 2014 and 2015 was Jupiter and CL111, respectively. Rice was drill-seeded at 359

seed m<sup>2</sup> to a depth of 1.27 cm on 21 April, 2014 and 31 March, 2015 using an Almaco heavy-duty grain drill (Almaco, Iowa) equipped with double-disk openers. Preflood Zn fertilizer treatments and Urea (460 g N kg<sup>-1</sup>) were surface broadcast as a single pre-flood application at the 4- to 5-leaf stage of rice development. Fields were flooded to a depth of approximately 10 cm after N fertilization and maintained until rice reached physiological maturity. Standard agronomic and pest management practices were conducted during the growing season based on state recommendations (Harrell et al., 2015).

Aboveground plant samples were hand harvested from a 0.9 m linear row of the middle drill-row at 50% heading to determine plant biomass and total Zn uptake. The plant samples were dried at 60°C in a forced air drier oven until uniform weights were attained. Samples were ground using a Wiley grinder and sieved through a 1-mm mesh sieve. A 0.5 g of ground subsample was digested for total elemental concentration. Elemental concentrations in the extract were measured using inductively coupled plasma atomic emission spectroscopy. Individual rice plots were harvested using a Wintersteiger Delta Combine (Wintersteiger, Inc., Salt Lake City, UT 84116-2876) equipped with a HM800 Harvest Master Grain Gauge system (Juniper Systems, Inc., Logan, UT, USA). Rough grain yield was adjusted to a moisture content of 120 g kg<sup>-1</sup>.

#### 4.2.4 Statistical Analysis

Data analysis was performed as randomized complete block design using SAS 9.4 (SAS Institute, 2013). Analysis of variance was performed using PROC MIXED procedure to examine the effect of Z fertilizer treatments and year on aboveground biomass, Zn uptake, rice grain yield, and tissue elemental concentration. Zn fertilizer treatment and year were considered fixed effects while replication was considered a random effect. Treatment means were separated using the Tukey multiple comparison test at  $\alpha = 0.05$ .



## 4.3 Results and discussion

### 4.3.1 Grain Yield

In 2014, Zn fertilization had no significant ( $P = 0.4024$ ) effect on rice grain yield. Compared to the unfertilized plots, Zn fertilization reduced rice grain yield for all fertilized plots except plots that received 2.8 kg Zn ha<sup>-1</sup> starter fertilizer without preflood fertilization (Table 4.3). This observation is in sharp contrast to what is commonly documented in literatures (Mandal et al., 2000; Chaudhary et al., 2007; Fageria et al., 2011). Response of rice cultivated under flooded conditions has been reported widely. Slaton et al. (2005b) and Fageria et al. (2011) reported 12 – 180% and 90% increases in grain yield as a result of Zn fertilization. Nonetheless, the lack of grain response to Zn in rice has been documented in fields fertilized with zinc sulfate (Slaton et al., 2005a). Authors reported that floret sterility may have partly accounted for the lack of grain yield response to zinc fertilization. Studies have reported that lack of zinc response indicates that there might have been adequate levels of plant available Zn in soil (Harrell and Saichuck, 2016). Grain yield was not significantly different among Zn fertilizer starter and preflood combinations (Table 4.3). This observation agrees with study by Shivay et al. (2015) in which authors did not notice significant difference in grain yield between ZSCU and other Zn fertilizer treatment. Slaton et al. (2005a) also did not observe difference in grain yield among zinc sulfate, Zn lignosulfaonate, and Zn oxy-sulfate Zn source. In contrast, Naik and Das, (2007), reported that plant fertilized with Zn EDTA significantly out-yield those fertilized with zinc sulfate. The highest rice grain yield (11656 kg ha<sup>-1</sup>) was observed in the plots fertilized with 2.8 kg Zn ha<sup>-1</sup> starter rate without preflood fertilization which was 439 kg ha<sup>-1</sup> greater as compared to unfertilized plot. However, grain yield at this Zn fertilizer combination was statistically similar to all Zn fertilizer treatments. Grain yield from plots without preflood Zn fertilization was

higher compared to ZSCU or urea: ZSCU blend at each Zn starter treatments. Luxury consumption of Zn has not been reported to decrease grain yield. Grain yield for pre-flood treatment within each starter rate was in the decreasing order 0 > 2:1 urea: ZSCU > 1:1 urea: ZSCU > ZSCU. It can therefore be inferred that Zn fertilization may have some deleterious affected grain yield. Grain yield at 1.12 starter fertilizer rate ranged from 10760 to 11210 kg ha<sup>-1</sup> across pre-flood fertilizer treatments. When starter application rate was increased to 2.8 kg Zn ha<sup>-1</sup>, the grain yield ranged from 10796 to 11656 kg ha<sup>-1</sup> which was slightly higher than 1.12 kg Zn ha<sup>-1</sup> starter treatment. The grain yield for 5.6 kg Zn ha<sup>-1</sup> starter rate ranged from 10744 – 10973 kg ha<sup>-1</sup> across pre-flood treatments which was lower compared to 1.1 and 2.8 kg Zn ha<sup>-1</sup> starter rates.

Grain yield from Zn fertilized plots did not significantly vary ( $P = 0.6865$ ) from plots without any Zn fertilization in 2015 (Table 4.4). Grain yield at the 2015 site (9616 – 10371 kg ha<sup>-1</sup>) was lower compared to those observed in 2014 (Table 4.3 and 4.4). The highest grain yield (10371 kg ha<sup>-1</sup>) was observed at the unfertilized plots which did not receive any Zn. Similar to what was observed in 2014, grain yield was numerically higher for rice plants harvested from unfertilized Zn plots compared to all other plots but the difference was not significant (Table 4.4). This suggests that plant available Zn in the soil (1.7 kg ha<sup>-1</sup>) was sufficient to meet the plant Zn needs and this may have masked the potential response of Zn fertilization. Grain yield at the 1.12 kg Zn ha<sup>-1</sup> starter rate for 0, 2:1 Urea: ZSCU, 1:1 Urea: ZSCU, and ZSCU were 10076, 10102, 10015, and 9780 kg ha<sup>-1</sup>, respectively. When starter rate was increased to 2.8 kg Zn ha<sup>-1</sup>, grain yield for 0, 2:1 Urea ZSCU, 1:1 Urea: ZSCU, and ZSCU were 9912, 9909, 9847, and 9616 kg ha<sup>-1</sup>, respectively. Grain yield was higher for 1.12 kg ha<sup>-1</sup> compared to 2.8 kg ha<sup>-1</sup> starter rate at the same pre-flood treatments. The grain yield at the 5.6 kg Zn ha<sup>-1</sup> starter application rate for

0, 2:1 Urea: ZSCU, 1:1 Urea: ZSCU, and ZSCU were 10332, 9672, 10181, and 10297 kg ha<sup>-1</sup>, respectively. The yield from at this starter rate was numerically higher compared to 2.8 kg Zn ha<sup>-1</sup> but similar to 1.12 kg Zn ha<sup>-1</sup>. Grain yield for preflood treatments generally decreased in the order 0 > 2:1 Urea: ZSCU > 1:1 Urea: ZSCU > ZSCU which correspond to increasing Zn application rate.

#### 4.3.2 Aboveground Biomass

Rice biomass was harvested at 50% heading stage. Biomass response to Zn fertilization varied significantly ( $P < 0.0001$ ) among years as a result of differences general environmental condition. Higher rainfall, low disease and weed pressure in 2014 may have partly contributed to a better rice growth and development. Consequently, the biomass data is presented and discussed separately for each year. Plants in the unfertilized plots did not exhibit typical Zn deficiency symptoms such as bronzing and stunted growth for both years (Sharma et al., 2013). There were no visible growth differences between rice from fertilized and unfertilized plots. The effect of zinc fertilizer treatments on biomass in 2014 is shown in Table 4.3. Biomass ranged from 13737 to 15938 kg ha<sup>-1</sup> in 2014. Analysis of variance showed that biomass from unfertilized plots was statistically similar ( $P = 0.7017$ ) to all the fertilized plots with Zn (Table 4.3). Fertilizing soil with Zn at the recommended rate provided slightly increased biomass over the unfertilized plots; however, this increase was not significant. The biomass of rice plant from plots which received Zn application were the same as the plants from unfertilized plots, suggesting that soil Zn concentration was not limiting to influence biomass between planting and 50% heading. The critical level of Mehlich III extractable Zn for rice cultivated on rice soils in Louisiana varies from 1.5 – 2 mg Zn kg<sup>-1</sup> depending on soil pH (Harrell and Saichuck, 2016). In current trial, the soil test Zn from the control plot (2.4 mg Zn kg<sup>-1</sup>) was greater than the critical level, suggesting

that the soil supplied sufficient amount of zinc required for optimal rice growth and development. The high biomass from unfertilized plot ( $14368 \text{ kg ha}^{-1}$ ) is in contrast to previously published results (Hafeez et al., 2012). Nonetheless, biomass response of lowland rice to zinc addition from zinc sulfate and zinc sulfate coated applied independently has been reported by Shivay et al. (2015). The authors reported that application of  $2.83 \text{ mg Zn kg}^{-1}$  using ZSCU and zinc sulfate as a zinc source resulted in 11 and 9% increase in biomass over unfertilized plots, respectively. The initial Zn concentration in the soil prior to the trial was  $0.35 \text{ mg Zn kg}^{-1}$  with the critical level ranging from  $0.36 - 0.90 \text{ mg Zn kg}^{-1}$ .

Based on analysis of variance, the biomass between Zn fertilizer treatments in 2014 was not significantly difference ( $P = 0.7017$ ), although response was expected based on the low initial soil test Zn results prior to the selection of study site (Table 4.3). Biomass from plots managed under split application of Zn fertilizer as starter and preflood treatments were similar to the recommended application rate. Similar results were observed by Naik and Das, (2007) where split application of zinc sulfate did not show significant difference in biomass compared to a single application rate. The best possible explanation for the above observation is that the soil supplied reasonable amount of Zn. Prior to selection of study site for this trials and several other trials, the soil samples were collected showed that zinc was limiting in the soil. However, the Zn concentration from soil samples were collected from the control plots just before starter fertilizers were applied showed that Zn was sufficient. The result in this study is in contrast to what was reported in other studies. Shivay et al. (2015) observed that significant difference in biomass with increasing Zn application rate. Among the preflood Zn treatments evaluated in 2014, biomass from plots fertilized with ZSCU was numerically greater compared to the urea: ZSCU blends at  $1.12$  and  $2.8 \text{ kg Zn ha}^{-1}$  starter rates (Table 4.3). However, at  $5.6 \text{ kg Zn ha}^{-1}$

starter rate, biomass was higher for 2:1 Urea: ZSCU compared to the other preflood Zn f treatments. The biomass from preflood Zn treatment at all the starter rates was lower than the recommended rate with the exception of 2:1 urea: ZSCU blend and ZSCU at 5.6 and 2.8 kg Zn ha<sup>-1</sup>, respectively. Since Zn was not limiting, the impact of experimental ZSCU fertilizers were not drastically observed in 2014. However, the relative high biomass from these fertilizers in comparison to the remaining preflood treatment suggests that ZSCU can influence biomass.

Biomass from unfertilized plots were statistically similar ( $P = 0.5389$ ) to plots with the Zn fertilization in 2015 and hence Zn fertilization did not influence biomass. Although this trial was conducted in a different site, the lack of difference in fertilizer treatment was similar to what was observed in 2014 (Table 4.4). Table 4.1 shows that soil Zn levels in control plot just before starter application were adequate (1.7 kg Zn ha<sup>-1</sup>) and this may partly explain the lack of difference in biomass of plants from between the fertilized and unfertilized plots (Harrell and Saichuck, 2016). The average biomass after Zn fertilization in 2015 is presented in Table 4.4. Mean biomass for Zn fertilizer treatments ranged from 6081 to 7894 kg ha<sup>-1</sup> in 2015. In comparison to 2014, the biomass for all Zn fertilizer treatments was lower in 2015. Preflood application of 2:1 urea: ZSCU blend had higher biomass compared to the other preflood treatments at the same starter rate. Biomass from plots fertilized with 2:1 urea: ZSCU increased biomass by 7 – 17% compared to unfertilized plots. Also, the 2:1 urea: ZSCU had 11 – 20% increase in biomass over the recommend starter application. The relatively high biomass from urea: ZSCU blend could be attributed to better Zn distribution compared to the other preflood treatment.

### 4.3.3 Zinc Uptake

Plant uptake of Zn was estimated by determining Zn concentration in the whole above ground biomass. Zn uptake ranged from 47.4 – 92.4 kg Zn ha<sup>-1</sup> in 2014. Analysis of variance showed significant ( $P < 0.0001$ ) effect of Zn fertilizer treatment on Zn uptake in 2014. Zn application at the highest starter rate significantly increased Zn uptake by rice with the exception of plots with no preflood Zn treatment (Table 4.3). The highest Zn uptake of 92.4 kg ha<sup>-1</sup> in 2014 was obtained with the application of 5.6 kg Zn ha<sup>-1</sup> starter fertilizer and 1:1 Urea: ZSCU preflood fertilizer combination which was 49% greater compared to the unfertilized plots (Table 4.3). At 1.12 kg Zn ha<sup>-1</sup> starter rate, Zn uptake for 0, 2:1 Urea: ZSCU, 1:1 Urea: ZSCU, and ZSCU were 50.3, 65.4, 58.1, and 66.4 kg ha<sup>-1</sup>, respectively. When starter rate was increased to 2.8 kg Zn ha<sup>-1</sup>, Zn uptake at 0, 2:1 Urea: ZSCU, 1:1 Urea: ZSCU, and ZSCU were 57.2, 66.4, 70.4, and 87.2 kg ha<sup>-1</sup>, respectively. The Zn uptake at 2.8 kg Zn ha<sup>-1</sup> was numerically higher than unfertilized plots as well as all the preflood treatments at 1.12 kg Zn ha<sup>-1</sup>. All the preflood treatment except 0, significantly increased Zn uptake at 5.6 kg Zn ha<sup>-1</sup> starter rate compared to the unfertilized plots with 2:1 Urea: ZSCU (92.4 kg ha<sup>-1</sup>), having a higher Zn uptake than the other preflood treatments (Table 4.3). With the exception of ZSCU, the Zn uptake the preflood application rate at 5.8 starter rate was higher than those from 1.12 and 2.8 kg Zn ha<sup>-1</sup> starter rates. Zn uptake by plants did not vary significantly between preflood treatments at each starter rate. The Zn uptake by plants fertilized with ZSCU as a preflood treatment higher than the other preflood treatment at 1.12 and 2.8 kg Zn ha<sup>-1</sup> starter rate while plots fertilized with 2:1 urea: ZSCU had the highest Zn uptake at the 5.6 kg Zn ha<sup>-1</sup> starter rate. The high uptake of Zn in ZSCU preflood treatment was expected considering the amount of Zn applied was higher compared to the other preflood treatment (Table 4.2). Generally, Zn uptake increased with increasing Zn application rate within

each starter rate. Several studies have reported that Zn uptake by rice corresponds with the amount of Zn applied even when responses to biomass and grain yield are not observed (Hafeez et al., 2013).

Zn uptake by rice plant did not differ significantly ( $P = 0.2910$ ) among Zn fertilizer treatments in 2015. The least ( $31.5 \text{ kg ha}^{-1}$ ) and highest ( $45.5 \text{ kg ha}^{-1}$ ) Zn uptake in 2015 occurred in plots fertilized with  $5.6 \text{ kg Zn ha}^{-1}$  starter fertilizer with no pre-flood fertilization and  $5.6 \text{ kg Zn ha}^{-1}$  starter fertilizer with 2:1 urea: ZSCU, respectively. The Zn uptake at  $1.12$  for 0, 2:1 urea: ZSCU, 1:1 urea: ZSCU, and ZSCU were  $40.8$ ,  $40.8$ ,  $32.3$ , and  $34.3 \text{ kg ha}^{-1}$ , respectively. The Zn uptake at this starter rate was higher than unfertilized plots with the exception of 1:1 urea: ZSCU. The Zn uptake at  $2.8 \text{ kg Zn ha}^{-1}$  for 0, 2:1 urea: ZSCU, 1:1 urea: ZSCU, and ZSCU were  $37.3$ ,  $37.0$ ,  $35.8$ , and  $38.3 \text{ kg ha}^{-1}$ , respectively. The Zn uptake at this starter rate was higher than unfertilized plots and the recommended application rate. The Zn uptake at  $5.6 \text{ kg Zn ha}^{-1}$  for 0, 2:1 urea: ZSCU, 1:1 urea: ZSCU, and ZSCU were  $31.5$ ,  $45.5$ ,  $38.3$ , and  $41.3 \text{ kg ha}^{-1}$ , respectively. The zinc uptake for pre-flood treatment at this starter rate was numerically higher compared to similar pre-flood treatment at  $1.12$  and  $2.8 \text{ kg Zn ha}^{-1}$  with the exception of the 0 pre-flood treatments.

#### 4.3.4 Tissue Elemental Concentration

The tissue elemental concentration of biomass harvested at 50% heading in 2014 is shown in Table 4.5. The tissue Zn concentration ranged from  $33.1$  to  $62.3 \text{ mg Zn ha}^{-1}$  in 2014. The range of Zn concentration in this study were within or higher than the sufficiency range for rice, indicating that Zn was not limiting in current study even for unfertilized plot (Jones et al., 1996). Tissue Zn concentration were significantly influenced by Zn fertilization during 2014 ( $P < 0.001$ ). The tissue Zn concentration for all Zn treatments increased as Zn fertilizer rate

increased from 1.1 to 12.5 kg Zn ha<sup>-1</sup> (Table 4.5). Tissue Zn concentration at 1.12 kg Zn ha<sup>-1</sup> starter rate for 0, 2:1 Urea ZSCU, 1:1 Urea ZSCU, and ZSCU were 35.3, 44.0, 42.4, and 43.6 mg Zn ha<sup>-1</sup>, respectively. When 2.8 kg Zn ha<sup>-1</sup> starter fertilizer was applied, tissue Zn concentration at 0, 2:1 urea: ZSCU, 1:1 urea: ZSCU, and ZSCU were 40.7, 46.8, 48.0, and 54.8 mg Zn kg<sup>-1</sup>, respectively. Tissue Zn concentration at 2.8 kg Zn ha<sup>-1</sup> was numerically higher compared to unfertilized plots as well as all the preflood treatments at 1.12 kg Zn ha<sup>-1</sup> but the differences was not significant. Tissue Zn concentration at 5.6 kg Zn ha<sup>-1</sup> starter rate for 0, 2:1 Urea ZSCU, 1:1 Urea ZSCU, and ZSCU were 45.1, 51.8, 62.3, and 54.7 mg Zn kg<sup>-1</sup>, respectively. With the exception of 0 kg Zn ha<sup>-1</sup> preflood treatments, tissue Zn concentration for all the preflood treatments was significantly higher than the unfertilized plots. However it was similar to the other preflood treatment at the 1.12 and 2.8 kg Zn ha<sup>-1</sup> starter rate. The concentrations of the other elements were within the sufficiency range for rice and hence, these elements were not limiting. Also there was no significant difference in tissue concentrations among Zn fertilizer treatments. This is contrary to what has been documented in other studies that showed that high Zn concentration tend to decrease P uptake and subsequently P tissue concentrations (Shivay et al., 2015). A close relationship between Zn and other element such as Fe, P, and K has been reported by Shivay et al. (2015). Even at the highest Zn application rate, the tissue concentrations of other element were comparable to those in unfertilized plots.

The tissue elemental concentration of biomass at 50% heading in 2015 for the various Zn fertilizer treatment combinations are presented in Table 4.6. Addition of Zn did not significantly increase tissue Zn concentration over unfertilized plots in 2015 as observed in 2014. Tissue Zn was similar between preflood Zn treatments within each starter application rate. The tissue



concentration of the other elements did not vary significantly with Zn fertilization as reported in previous studies.

Table 4.3 The effect of Zn fertilization treatment on biomass, rice grain yield, and Zn uptake in 2014.

Starter rate	Preflood treatment			
		Biomass	Grain yield	Zn uptake
		-----kg ha <sup>-1</sup> -----		
0	0	14368 a	11217 a	47.4 d
1.12	0	14308 a	11210 a	50.3 cd
	2:1 Urea: ZSCU	14955 a	10795 a	65.4 a-d
	1:1 Urea: ZSCU	13737 a	10842 a	58.1 b-d
	ZSCU	15346 a	10760 a	66.4 a-d
2.8	0	13937 a	11656 a	57.2 b-d
	2:1 Urea: ZSCU	14082 a	11185 a	66.4 a-d
	1:1 Urea: ZSCU	14690 a	10807 a	70.4 a-d
	ZSCU	15938 a	10796 a	87.2 ab
5.6	0	14801 a	10973 a	67.2 a-d
	2:1 Urea: ZSCU	15728 a	10837 a	81.4 abc
	1:1 Urea: ZSCU	14932 a	10810 a	92.4 a
	ZSCU	15092 a	10744 a	82.2 ab
11.2	0	15555 a	10764 a	84.8 ab
<i>P</i> (0.05)		0.7017	0.4024	<0.0001

Preflood zinc concentration supplied by ZSCU, 1:1 Urea ZSCU, and 2:1 Urea ZSCU were 6.86, 3.2 and 2.1 kg Zn, respectively.

Table 4.4 The effect of Zn fertilization treatment on biomass, rice grain yield, and Zn uptake in 2015.

Starter rate	Preflood treatment	Biomass	Grain yield	Zn uptake
		-----kg ha <sup>-1</sup> -----		
0	0	6858 a	10371 a	32.8 a
1.12	0	7848 a	10076 a	40.8 a
	2:1 Urea: ZSCU	7894 a	10102 a	40.8 a
	1:1 Urea: ZSCU	5998 a	10015 a	32.3 a
	ZSCU	6487 a	9780 a	34.3 a
2.8	0	6859 a	9912 a	37.3 a
	2:1 Urea: ZSCU	7343 a	9909 a	37.0 a
	1:1 Urea: ZSCU	6684 a	9847 a	35.8 a
	ZSCU	6679 a	9616 a	38.3 a
5.6	0	6081 a	10332 a	31.5 a
	2:1 Urea: ZSCU	8270 a	9672 a	45.5 a
	1:1 Urea: ZSCU	7446 a	10181 a	38.3 a
	ZSCU	7638 a	10297 a	41.3 a
11.2	0	6585 a	9865 a	35.8 a
<i>P</i> (0.05)		0.5389	0.6865	0.2910

Preflood zinc concentration supplied by ZSCU, 1:1 Urea ZSCU, and 2:1 Urea ZSCU were 6.86, 3.2 and 2.1 kg Zn, respectively.

Table 4.5 Mean tissue concentration of above ground biomass at 50% heading for starter and preflood zinc fertilization treatments in 2014.

Starter rate	Preflood treatment	Total extractable elemental concentration									
		P	K	Ca	Mg	S	Al	Fe	Mn	Zn	Cu
		-----g kg <sup>-1</sup> -----					-----mg kg <sup>-1</sup> -----				
0	0	2.7	9.5	2.9	2.2	1.6	228	385	688	33.1d	2.2
1.12	0	3.0	10.4	3.0	2.3	1.7	207	389	705	35.3cd	2.4
	2:1 Urea: ZSCU	3.0	10.4	3.2	2.4	1.9	193	410	751	44.0b-d	2.5
	1:1 Urea: ZSCU	2.8	9.8	3.1	2.2	1.7	131	311	735	42.4b-d	2.3
	ZSCU	3.0	10.2	3.0	2.2	1.6	113	286	642	43.6b-d	2.4
2.8	0	3.1	10.3	3.2	2.4	1.7	129	309	662	40.7b-d	2.4
	2:1 Urea: ZSCU	3.1	10.2	3.0	2.2	1.7	115	359	662	46.8a-d	2.3
	1:1 Urea: ZSCU	3.4	11.0	3.0	2.4	1.7	208	402	684	48.0a-d	2.4
	ZSCU	3.2	9.3	3.0	2.3	1.7	177	402	650	54.8ab	2.2
5.6	0	3.2	10.8	2.9	2.2	1.6	174	265	675	45.1b-d	2.3
	2:1 Urea: ZSCU	3.2	10.7	3.1	2.4	1.8	162	402	660	51.8a-c	2.6
	1:1 Urea: ZSCU	3.1	9.8	3.2	2.4	1.8	201	413	701	62.3a	2.6
	ZSCU	3.3	10.3	3.1	2.4	1.8	225	416	657	54.7ab	2.5
11.2	0	3.3	10.1	3.0	2.3	1.7	200	374	600	54.7ab	2.4
<i>P</i> (0.05)		0.2646	0.3965	0.9460	0.7442	0.6323	0.7775	0.8855	0.5208	<.0001	0.8821

Preflood zinc concentration supplied by ZSCU, 1:1 Urea ZSCU, and 2:1 Urea ZSCU were 6.86, 3.2, and 2.1 kg Zn, respectively.

Table 4.6 Mean tissue concentration of above ground biomass at 50% heading for starter and preflood zinc fertilization treatments in 2015

Starter rate	Preflood treatment	Total extractable elemental concentrations									
		P	K	Ca	Mg	S	Al	Fe	Mn	Zn	Cu
		-----g kg <sup>-1</sup> -----					-----mg kg <sup>-1</sup> -----				
0	0	3.3	12.9	2.2	2.0	1.5	91	161	791	47.8	2.4
1.12	0	3.4	11.7	2.2	2.1	1.5	103	179	838	51.8	2.4
	2:1 Urea: ZSCU	3.4	12.0	2.3	2.2	1.6	109	180	837	51.8	2.4
	1:1 Urea: ZSCU	3.5	12.5	2.4	2.2	1.7	107	188	803	54.0	2.6
	ZSCU	3.6	12.4	2.3	2.2	1.7	106	180	811	53.0	2.6
2.8	0	3.6	13.6	2.4	2.2	1.7	119	200	928	55.5	3.8
	2:1 Urea: ZSCU	3.4	11.9	2.3	2.1	1.6	88	166	805	51.3	2.4
	1:1 Urea: ZSCU	3.5	12.5	2.2	2.2	1.7	87	166	733	53.5	2.4
	ZSCU	3.6	12.4	2.3	2.4	1.9	103	166	836	57.0	2.8
5.6	0	3.5	13.7	2.3	2.1	1.6	85	151	784	52.3	2.5
	2:1 Urea: ZSCU	3.3	11.7	2.4	2.2	1.6	130	199	769	54.5	2.2
	1:1 Urea: ZSCU	3.5	12.2	2.5	2.4	1.7	113	195	827	51.8	2.6
	ZSCU	3.3	11.8	2.3	2.2	1.6	121	194	751	53.8	2.3
11.2	0	3.3	12.5	2.3	2.2	1.6	121	193	858	54.5	3.0
<i>P</i> (0.05)		0.7439	0.6918	0.6654	0.3890	0.1556	0.9226	0.9365	0.5738	0.5446	0.4014

Preflood zinc concentration supplied by ZSCU, 1:1 Urea ZSCU, and 2:1 Urea ZSCU were 6.86, 3.2 and 2.1 kg Zn, respectively.

#### **4.4 Conclusions**

The goal of this study was to determine if split application ZSCU fertilizer can be a viable alternative to single starter application of Zn sulfate. Generally, Zn fertilizers are applied as starter fertilizer because Zn deficiency symptoms occur during the 2- leaf stage of plants. However, the high N content (39%) in ZSCU fertilizers limits the amounts of Zn that can be applied by these experimental fertilizers to a maximum of 1.1 kg ha<sup>-1</sup>. Consequently to evaluate ZSCU as a Zn source require split application. Results from study showed that zinc uptake varied significantly among Zn fertilizer treatments in the first year of study. Preflood application of Zn showed beneficial effects on Zn uptake compared to those without fertilization within the same starter application rate. The relatively higher preflood Zn uptake suggests that larger granule size of ZSCU influence fertilizer distribution and hence Zn availability. Zinc uptake at the combination of the highest starter rate and preflood Zn fertilization was significantly higher compared to the unfertilized plots. Also, Zn uptake from all plots fertilized with the combination of starter and preflood application of ZSCU were similar to the recommended practice of single starter application of Zn sulfate. It can therefore be inferred that the solubility and hence plant availability of experimental fertilizers were similar to zinc sulfate. On the basis of Zn uptake, experimental ZSCU can be a Zn fertilizer source but the enhancement in Zn uptake did not translate to biomass and grain yield increase. The outcome of this study supports other studies that showed that ZSCU influences Zn nutrition but not grain yield and biomass. In conclusion, application of ZSCU as a Zn source was as effective single starter application of Zn sulfate in drill seeded rice production.

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## Chapter 5. Conclusions

Multiple approaches to minimizing ammonia volatilization from urea in flooded rice fields have been evaluated and several have been adopted with varying degrees of success. The most cost effective strategy is to establish the permanent flood in less than three days is hampered by the irrigation capacity of many commercial rice farms in Louisiana. Treatment of urea with NBPT and/or NPPT is an industry standard for controlling ammonia volatilization when fields cannot be flooded in a timely manner because of their consistent effectiveness across different soil types and environmental conditions. Zinc deficiency is another major soil fertility constraint commonly encountered by rice producers primarily because of low inherent soil Zn which can be further aggravated by establishing the permanent flood when rice plants are already showing deficiency symptoms. A single fertilizer product that can supply both N and Zn while also minimizing ammonia volatilization losses and improving Zn distribution would be economically and environmentally beneficial to rice producers impacted by these soil fertility constraints. This rationale prompted the need for this novel approach to control ammonia volatilization and also supply Zn using a ZSCU granulated fertilizer.

A study was conducted on four important rice soils in Louisiana to ascertain the ammonia volatilization control of four experimental zinc sulfate coated urea fertilizers in a closed environment (ZSCU). The experimental ZSCU fertilizers were compared to urea and urea treated with three rates of NBPT. Ammonia volatilization from urea varied significantly among soils ranging from 14 – 27.5% during the 14 d trial. Ammonia volatilization from urea was lower on soils with lower pH and higher cation exchange capacity. Urea treated with NBPT drastically reduced ammonia volatilization during the 14 d trial by 27 – 63% across soils and NBPT application rates as compared to untreated urea. More importantly, the inhibitory effect of NBPT

on ammonia volatilization was consistent across soils with the exception of the lowest NBPT application rate ( $0.3 \text{ g kg}^{-1}$ ). The inhibitory effect of some of the experimental ZSCU on ammonia volatilization was not consistent across all soils. Experimental ZSCU fertilizers with the physical coating only were only effective in soils which had the highest higher ammonia volatilization losses from urea. Experimental fertilizers containing B, NBPT, and the calcium sulfate coating, reduced ammonia volatility by 30 – 81% and were effective in minimizing ammonia volatilization regardless of soil type. Ammonia volatilization losses from experimental ZSCU fertilizers containing NBPT were similar or lower than those from the commercial recommended NBPT ( $0.9 \text{ g kg}^{-1}$ ) rate used in this study. The closed environment study showed that the experimental ZSCU containing B with or without NBPT fertilizer can effectively minimize ammonia volatilization across different soil types.

Field studies were conducted to evaluate ammonia volatility potential of experimental ZSCU fertilizers on a Crowley silt loam, a common soil for rice cultivation in southwest Louisiana. The cumulative ammonia volatilization from urea was 15.0 and 22.5% in 2014 and 2015, respectively. Urea treated with NBPT reduced urea volatilization losses by 80 and 76% in 2014 and 2015, respectively. The experimental ZSCU fertilizers were most effective in controlling ammonia volatilization in 2015. The physical coating with zinc sulfate alone reduced ammonia volatilization 24% in comparison to urea in 2015. The addition of B to the physical coating had an additive effect in reducing ammonia volatilization, whereas when ZSCU in combination with NBPT and B did not provide additive effect over physical coating alone. The inhibitory effects observed in the controlled experiment were not evident during the field trial. Despite the addition of urease inhibitors, the experimental fertilizers showed inconsistencies commonly associated with controlled release fertilizers in minimizing ammonia volatilization.

Ammonia volatilization control was greater for urea treated with NBPT than the experimental ZSCU fertilizers evaluated in this trial. In the first year of study, the differences in ammonia volatilization did not influence biomass and nitrogen use efficiency. Rice plants fertilized with NBPT treated urea or the experimental ZSCU fertilizers 10 d prior to permanent flood establishment both had similar biomass yield and NUE as those fertilized with urea. Grain yield was similar among all N fertilizer treatments at 135 kg N ha<sup>-1</sup>. In the second year, biomass was similar for all N fertilizer sources; however, urea treated with NBPT out yielded all other N fertilizers. The results suggest that the experimental ZSCU fertilizers may reduce ammonia volatilization in some years but may not impact grain yield.

One of the experimental ZSCU fertilizers was evaluated as a potential Zn source in rice. The field experiment was carried out for two years at different sites on a Mowata silt loam. The soil test prior to the selection of trial site indicated that Zn was limiting. In this trial, 14 Zn fertilizer treatments were evaluated. The Zn fertilizer treatments were a combination of starter with or without preflood application. The starter rates were 0, 1.12, 2.8, 5.6, and 11.2 kg Zn ha<sup>-1</sup> using zinc sulfate. Preflood Zn fertilization was then carried out during the 4 – 5 leaf stage of rice seedling within 1.12, 2.8, 5.6 starter rates. The preflood treatments were 0, 2:1 urea: ZSCU, 1:1 urea: ZSCU, and ZSCU. A Zn yield and biomass response was not observed either year however, an increase in Zn uptake was observed in 2014. Results from study suggest that the effect of split application of zinc sulfate and ZSCU was comparable to the single application of zinc sulfate which is commonly recommended practice.

In conclusion, experimental ZSCU fertilizers showed the ability to reduce ammonia volatilization, particularly in soils or under conditions when ammonia volatilization potential from urea is high. The inconsistencies in their performance make ZSCU fertilizers unreliable as

compared to urea treated with NBPT. The ZSCU fertilizers did prove to be an equally effective Zn fertilizer source in rice as compared to granular zinc sulfate.

## **Vitae**

Nutifafa Adotey was born and raised in Ghana, West Africa. He graduated from University of Ghana with BSc. Agriculture (Soil Science). Upon completion, he graduated with M.S. in General Agriculture from Stephen F. Austin State University in 2013 under the direction of Dr. Leon Young. In 2013, he was accepted into School of Plant, Environmental and Soil Science at Louisiana State University. He anticipates graduating with a Ph.D. Degree in Plant, Environmental Management and Soil Science in December 2016 under the guidance of Dr. Dustin Harrell.